

ASD TECHNICAL REPORT 61-322

AD0264193

OFFICIAL PROJECT
RECORD COPY

ASRCNP

C-19

OFFICIAL FILE COPY

MATERIALS SYMPOSIUM

13-15 SEPTEMBER 1961

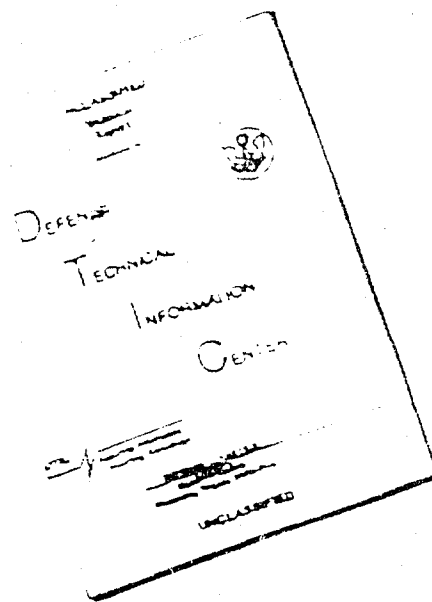
HOTEL WESTWARD HO
Phoenix, Arizona

JULY 1961

AERONAUTICAL SYSTEMS DIVISION

20040224179

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST
QUALITY AVAILABLE. THE COPY
FURNISHED TO DTIC CONTAINED
A SIGNIFICANT NUMBER OF
PAGES WHICH DO NOT
REPRODUCE LEGIBLY.

REPRODUCED FROM
BEST AVAILABLE COPY

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., for sale to the general public.

Copies of ASD Technical Reports and Technical Notes should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

MATERIALS SYMPOSIUM

13-15 SEPTEMBER 1961

HOTEL WESTWARD HO

Phoenix, Arizona

JULY 1961

Directorate of Materials and Processes

**AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

The increasingly rapid pace of modern technology throughout the world makes it imperative that our Air Force research programs be daringly imaginative and that our efforts include high risk items in order to accelerate progress. Weapon systems for the space ages of the future will be totally different from past and present types and will of necessity involve fantastically complex structures and components with greatly increased operational lifetimes and extremely high reliability. At the same time many more immediate problems must be solved. Such things as creep and fatigue in applications calling for long operational lifetimes, light weight structures for vertical takeoff or landing aircraft and high temperature tires must receive careful attention. These requirements cannot be met until materials scientists and engineers provide the essential ingredients for them. In order to meet the bare essentials of our programs, greatly accelerated progress in materials will be needed.

At the NATO Symposium on Materials Research which was held last June, it was pointed out that such efforts should follow two paths. First, somewhat empirical engineering will have to be continued with its attacks aimed at solving specialized and specific problems encountered in particular applications. Secondly, expanded use must be made of more fundamental studies involving chemistry and physics and other sciences and especially interdisciplinary research. All these efforts must be closely integrated to avoid delays.

The two previous meetings of this type were most helpful in providing the free exchange of ideas which can accelerate progress. It is expected that the papers presented here will be even more useful in conveying Air Force requirements to materials engineers and scientists throughout the defense community.



W.A. DAVIS
Major General, USAF
Commander

TABLE OF CONTENTS

	PAGE
SPACE ENVIRONMENT M.B. Gilbert, AFCRL	1
STRUCTURAL MATERIALS B. Chasman, ASD	8
A New Look at Superalloys Capt. L.F. Bubba, ASD	25
Structural Materials to 1800°F (Steel and Titanium) P.L. Hendricks, ASD	40
Graphite Capt. R.H. Wilson, ASD	57
Plastics, Adhesives, and Composite Materials F.W. Kuhn, G.P. Peterson, R.C. Tomashot, ASD	79
Protection of Refractory Metals Against Atmospheric Environments N.M. Geyer, ASD	101
Vapor Pressure Measurement P.W. Dimiduk, ASD	121
The Thermodynamics of Ablation Dr. E. Rutner, ASD	140
Meteoretics and Hypervelocity Studies A.K. Hopkins, ASD	152
Materials Information and Design Data D. Shinn, ASD	173
Elemental Micro Analysis H.M. Rosenberg, ASD	187
Chemical Analysis of Solid State Materials by Mass Spectrometry W.L. Baun, ASD	196
The Future of Analytical Chemistry Dr. L. Harrah, ASD	217
Molecular Weight Measurement Mary T. Ryan, ASD	221
Microwave Ferrites J.B. Brauer, N.O. Korolkoff, RADC	229

TABLE OF CONTENTS (Cont'd)

	PAGE
Hard Magnetic Materials Dr. K. Strnat, ASD	242
Soft Magnetic Metallic Materials J.C. Olson, ASD	252
ELECTRONIC MATERIAL REQUIREMENTS F.E. Wenger, AFSC	267
Dielectric Materials for Advanced Astronautic Weapons Systems W.G.D. Frederick, J.I. Wittebort, ASD	275
Some Aspects of New Polymers for Dielectrics Dr. G.F.L. Ehlers, ASD	289
Progress on the Research of Solid State Phenomena and Materials Capt. W. Metscher, ASD	296
Refractory Metals as Engineering Materials T.D. Cooper, ASD	307
Aerospace Working Fluids D.A. Kirk, Lt. J. Roth, H. Adams, ASD	339
Aerospace Lubricants H.W. Adams, ASD	356
Advanced Lubrication Techniques G.A. Beane, ASD	382
Elastomers Dr. W.E. Gibbs, W. R. Griffin, R. G. Spain, ASD	393
Thermal Emittance Measurements R. A. Winn, ASD	423
Environmental Considerations for Thermal Protective Coatings R.M. VanVliet, J.J. Mattice, ASD	436
Coatings for Temperature Control in Space Vehicles J.H. Weaver, Lt. C. Jacobs, ASD	456
Thermal Protection H. Marcus, ASD	470
Refractory Emissive Coatings L.N. Hjelm, Lt. USAF, ASD	482

TABLE OF CONTENTS (Cont'd)

	PAGE
The Effect of Radiation on Solid State Materials and Devices Dr. B. Manning, AFCRL	505
Radiation Chemistry R.E. Rondeau, 1/Lt. USAF, Dr. J. Radell, ASD	514
Radiation Effects on Materials in Space R.L. Hickmott, G.H. Griffith, O.L. Donlon, O.V.P. Sessoms, T.W. Bailey, ASD	532
Transparent Materials R. Wittman, ASD	541
Unique Metallic Materials and Techniques Lt. Col. E.M. Kennedy, Jr., 1/Lt. S.A. Worcester, Jr., ASD	563
Materials Problems in Dynamic Energy Conversion Systems G.E. Thompson, ASD	589
Types of Thermionic Power Converters and Current Materials Limitation Capt. E.F. Redden, ASD	602
Solar Cells in Space R.W. Runnels, ASD	609
Materials for Energy Conversion Systems B. Rubin, ASD	615
FLIGHT VEHICLE POWER D. Mortel, ASD	636
IMPROVING THE MUTUAL GUIDANCE AND SUPPORT BETWEEN THE FIELDS OF MATERIALS AND DESIGN W.R. Micks, Rand	651
Welding and Brazing Space Age Materials R. Bowman, ASD	661
Ceramics and Intermetallics I.D. Latva, ASD	679
Organic and Inorganic Fibrous Materials J.H. Ross, ASD	711
Applied Research Program for Nondestructive Methods Development R.R. Rowand, ASD	739

TABLE OF CONTENTS (Cont'd)

	PAGE
The Nondestructive Measurements of Surface Connected Discontinuities W.L. Shelton, ASD	757
Ablative Materials D.L. Schmidt, ASD	775
Extrusion of High Temperature Materials P.S. Duletsky, Capt. USAF, ASD	817
Theoretical Formability J. Bryars, ASD	833
The Mechanical Behavior of Materials R.T. Ault, I.K. Ebcioglu, D.M. Forney, Jr., R.F. Klinger, J.A. Roberson, K.D. Shimmin, and W.J. Trapp, ASD	845
Beryllium Research and Development S.S. Christopher, Lt. USAF, ASD	883
Materials for Molecular Electronics Elizabeth H. Tarrants, ASD	901

PARTICIPATING ORGANIZATIONS

Headquarter, Air Force Systems Command
Andrews Air Force Base
Washington 25, D. C.

Air Force Cambridge Research Laboratory
L. G. Hanscom Field
Bedford, Massachusetts

Rome Air Development Center
Griffiss Air Force Base
New York

Rand Corporation
1700 Main Street
Santa Monica, California

Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio

SPACE ENVIRONMENT

M.B. Gilbert

Air Force Cambridge Research Laboratories,

Introduction

I have been asked to do two things in this presentation: first, to give a "broad-brush" description of the natural space environment, and secondly, to define possible problem areas for materials exposed to that environment.

The first task will be attempted, although it is difficult to give even a broad-brush treatment of such a subject in 30 minutes.

The second task, however, will not be attempted. You are already well aware of problems posed for materials by micrometeorites, trapped radiation, and sputtering. These and others are implicit in the information to be presented. In keeping with our research mission, AFCRL's Geophysics Research Directorate will continue to provide data concerning the aerospace environment which can, in turn, be applied by other agencies as the basis for establishing design criteria.

Solar Phenomena

Knowledge of the solar radiation (both electromagnetic and corpuscular) is probably the single most important factor in establishing the natural space environment, since so many physical phenomena are caused, or directly affected, by solar emissions. It is worthwhile, therefore, to start a discussion of the aerospace environment with a physical description of solar activity and emissions.

Disturbances are always present on the sun, even when it is described as "quiet." While these disturbances have little effect on the total electromagnetic radiation emitted, some of them cause large increases in the flux at very short or very long wavelengths. In contrast to the electromagnetic radiation, corpuscular emission from the sun appears to be predominantly transient.

Sunspots occur in the photosphere. They invariably have strong magnetic fields. The total number of spots fluctuates in a fairly regular 11-year cycle which seems to derive from a more fundamental magnetic periodicity of about 23 years. Faculae, which are regions of enhanced white-light brightness in the photosphere, are not well understood, but they are among the first intimations of the development of an active region, and often persist for weeks after the sunspots have disappeared. Plages, which are bright clouds low in the chromosphere, also frequently precede the appearance of sunspots and persist afterward.

The top of the chromosphere is in continual eruption. Cloud-like prominences often appear over both active and undisturbed regions. Prominences are luminescent gas clouds which take various forms, such as large quiescent masses, active loops, and the fast jets called surges. In the latter, incandescent matter is seen to stream outwards with speeds of 100 to 200 km/sec and occasionally up to 1000 km/sec. Surges and loops are always indicators of great activity.

In an active region, the typical "quiescent" phenomena are occasionally punctuated by extraordinarily sudden and violent eruptive bursts. These outbursts consist of a complex sequence of events, of which the solar flare is the first, and usually the most conspicuous.

Although it is not yet possible to predict with certainty, the onset of a particular solar flare, indications exist of conditions favorable to their occurrence. Flares occur most frequently at times of maximum sunspot activity, and tend to occur in association with sunspot groups which have a complex pattern of positive and negative magnetic poles. Also, flares usually occur in centers which display loop and surge prominences and coronal hot spots (emissions in the 5694 Å line of Calcium XV). The firing of many small flares has good correlation with the probability that a large flare will occur.

There is some possibility that prediction of the precise time and location of a large solar flare may be possible one or two minutes in advance, on the basis of the sequence of radio noise, visible, Lyman-alpha, and x-ray emission from a disturbed area.

We do not yet have sufficient knowledge of solar processes to establish unique relationships between the observed characteristics of a specific solar event and subsequent disturbances in the vicinity of the earth. For example, some flares produce strong ionospheric reactions, knocking out radio communications over a whole hemisphere, while others which are apparently identical, merely produce an exciting solar spectacle. The explosive activities must be the result of some previous train of events in the active centers where they occur. A major goal of research in solar physics is to determine the nature of these precursory events, and discover characteristic features and processes that will identify various types of solar events with the kinds of disturbances they produce.

Solar Corpuscular Emission, Van Allen Zones, and Cosmic Rays

A considerable number of protons and electrons evaporate from the outer solar corona, a plausible estimate being 10^{33} protons and electrons per second. This estimate may be modified in view of recent observations, which indicate an elliptical, locally inhomogeneous corona that extends to 20 solar radii. The intermittent emission of high speed charged particles from active regions of the sun greatly increases the particle density.

Most of the particles emitted during a solar flare reach the earth's orbit about 24 hours after the onset of a sudden ionospheric disturbance, an abrupt increase of ionization probably caused by the short-wavelength component of the electromagnetic radiation emitted by the flare. There is evidence, however, that some particles reach the earth 65 minutes after the sudden ionospheric disturbance. The particles are channeled toward the auroral zones, and produce a widespread geomagnetic disturbance.

Corpuscular radiation can be trapped by the earth's magnetic field. The idealized contours of the Van Allen belts with inner and outer zones are familiar to all of you. The composition and energies of the trapped radiation are quite different in the two zones. The situation is not as simple, however, as the idealized picture indicates. More recent measurements show that the outer zone has not nearly so well defined a structure. The intensities and the distributions vary in time by large factors. For example, Explorers VI and VII revealed a complex sequence of depletion and enhancement of the particle population and shifts in the spatial distributions which occurred in association with magnetic storms. On one occasion (30 March 1960) the outer zone disappeared, or at least was reduced below the level of detection, for almost 24 hours.

Below the outer zone above North America, an increase of a factor of 10 in the counting rate has occurred on magnetically disturbed days. This is believed to be caused by the escape of particles from the outer zone due to the magnetic disturbances associated with a sudden ionospheric disturbance.

The inner zone appears to be comparatively stable. Very little, if any, change in radiation intensity in the inner zone has been observed during a magnetic storm.

There is general agreement on how the particles remain trapped, spiralling around the lines of force and being reflected back and forth between northern and southern hemisphere mirror points. It has been established that the protons in the inner zone are products of the decay of neutrons which move outwards from the top of the atmosphere. These neutrons are produced in nuclear disintegrations caused by cosmic ray interactions in the outer atmosphere. The low energy electrons, found primarily in the outer zone, are assumed to be of solar origin. This requires a disturbance of the earth's magnetic field which will allow the solar particles to become trapped. A detailed theory of this disturbance is still lacking.

The high-energy electrons in the outer belt are too energetic for solar particles, so that if they are of solar origin, a subsequent acceleration is required to account for the observed energies. No satisfactory mechanism has yet been proposed, but there are indications that the acceleration must take place near the earth.

It is an unhappy fact that the total corpuscular radiation near the earth as a function of position, direction, and time is not well known. Data on the time fluctuations, and particles with kinetic energy below 1 Mev, are especially needed.

During the last sunspot cycle, extensive systematic observations of cosmic radiation proved that at least the low energy part of the spectrum is strongly modified by the sun's action. Recent balloon flights have indicated a diurnal variation in the heavy primary component, which is a flux of nuclei completely stripped of their electrons.

The lower limit of kinetic energy is between 30 and 1 Mev, depending on time. The upper limit is at least 10^{10} Mev. Only particles with energy below 50 Mev seem to have a time variation of intensity. Different nuclei have roughly the same distribution of momentum per unit charge. The relative abundance in the primary flux is about 85 percent protons, 13 percent helium, and 2 percent heavier nuclei.

Observations made at the surface or even at great heights in the atmosphere do not provide unambiguous measurements of the primary cosmic rays, due to the presence of secondary radiation, produced by interactions with the atmosphere.

Cosmic ray intensity usually decreases greatly as solar activity increases. However, large anomalous increases also occur. Thus a sharp increase in intensity at high latitudes may follow a solar flare. This increase occurs from a few minutes up to about one and one-half hours after the flare, depending upon the particular flare, its position on the solar disk and its location with respect to the Earth. Although a large increase in intensity occurs at some high latitudes, little or none is found at low latitudes. The increase is apparently due to a large additional flux of solar particles, most of which have energy less than a few Mev.

During a solar flare, the neutron flux increases much more than does the charged particle flux. Even small solar flares produce a flux of penetrating particles which is estimated to be as much as 10^4 times that of the cosmic radiation. Thus the radiation from solar activity can at times be more important than the primary cosmic rays.

Corpuscular radiation can produce thermal effects by impact with the surface of a space vehicle. In regions of high particle densities and velocities, the contribution to the thermal input may be comparable to that of the solar thermal radiation in the vicinity of earth. For example, during times of high solar activity, solar winds of 10^5 particles/cm³ with radial velocities of 1500 km/sec have been postulated. If such a flux of protons strikes the vehicle the thermal input from absorption of their kinetic energy alone would be about 20 percent of the mean solar constant. This could seriously upset the thermal balance in the interior.

Measurements from Explorer X in March 1961 confirmed the existence of a solar wind. Preliminary analyses of data indicate a solar wind of 10 protons/cm³ traveling at speeds of about 275 km/sec during a quiet period, with the speed increasing to 1600 km/sec after a solar flare which occurred on 26 March 1926. On this basis, the thermal inputs would be on the order of 10^{-7} and 10^{-5} cal/cm²/min respectively.

Solar Electromagnetic Radiation

A value of 2 cal/cm²-min is generally accepted as the mean total energy of solar electromagnetic radiation at the earth's orbit, and the energy distribution is considered to be similar to blackbody emission at 6000°K.

It is difficult to determine the true spectral distribution of this radiation. Infrared spectra recently obtained indicate that at wavelengths beyond 5 microns, the radiation more closely approximates that of a blackbody at 5000°K. However, for the purpose of specifying the environment, radiation of wavelengths longer than 2000 Å is reasonably well known. For wavelengths of the extreme ultraviolet and the soft x-ray region, space experiments are just now providing necessary measurements of spectral distributions and intensity above atmospheric absorption. Compilations of solar radiations for wavelengths shorter than 3000 Å have been prepared, but these continue to require revision as additional and better experimental results become available.

Although less than 2 percent of the mean solar electromagnetic energy lies in the region below 3000 Å, we need more accurate information about these radiations because of their strong ionizing effects. The photoionization of any material exposed to direct solar ultraviolet and x-rays will depend strongly on the wavelengths as well as the total intensity. For example, the Helium II emission line at 304 Å has a great effect on the ionosphere, where it is almost entirely absorbed in the 150 to 200 km region by photoionizing the atmosphere. Recently, large daily variations in the density of the upper atmosphere have been discovered which are attributed to the energy supplied by absorption of this helium line.

Measurements of the quiet sun indicate that the average solar radiation at different radio wavelengths varies by a factor of three or more in a cycle similar to the sunspot cycle. Tremendous increases in the radio emission from small areas of the sun (up to hundreds of times the corresponding emission from the whole solar disk) are observed from regions associated with flares.

Fields

The general intergalactic field, in which the solar system is embedded, appears to have a strength of 10^{-5} to 10^{-6} gauss.

On a cosmic scale, the dipole field of the earth attenuates rapidly. Thus the magnetic field in interplanetary space will be governed by the field of the sun and the magnetic effects produced by solar corpuscular streams. These streams modify the sun's main field drastically, since the outward flowing ionized gas draws out the lines of force of the solar magnetic field in a radial direction. Also, components which are perpendicular to the velocity may be "frozen in," and carried radially out with the streams. Thus it is possible for the magnetic field to vary in time through a range of 10^{-2} to 10^{-8} gauss or more.

Our experimental knowledge of the geomagnetic field within and beyond the magnetosphere is meager. The magnetometer measurements on Explorer VI agreed with values predicted from calculations of the dipole moment up to about 5 radii from the center of the earth. Beyond this, however, systematic deviations began to appear which can be accounted for by postulating that at 7 to 10 earth radii there is a ring current of several million amperes which modifies the predicted magnetic field. Results from Pioneers I and V confirm the onset of systematic deviations at 5 radii. On the basis of space-probe data, the earth's field is now believed to terminate at 14 or 15 earth radii.

It is postulated that hydromagnetic waves are generated by changes in the pressure of the solar wind, and by instabilities at the boundary of the magnetosphere. In addition, changes in the size of the magnetosphere will also generate hydromagnetic waves.

When complete data from Explorer X becomes available, we will have a better understanding of these phenomena. Preliminary findings, released in April 1961, confirm the solar-wind hypothesis of the interplanetary magnetic field. This satellite detected disturbances in the interplanetary magnetic field for several hours before the appearance of a large solar flare. Field strength during the flare varied from 5 to 40×10^{-5} gauss. The sequence of magnetometer disturbances and positions of Explorer X, and the records of the sudden commencement geomagnetic disturbance on earth, seem to prove that the sudden commencement was caused by particles speeding from the sun at 1000 km/sec.

Drag and Sputtering

As an object moves through the earth's upper atmosphere at orbital velocities, it experiences various phenomena caused by interaction with ambient particles. A charge accumulation will result due both to the photoelectric effect and to collisions with electrons and positively charged ions. Phenomena such as recombination, surface accommodation, and the secondary emissions and sputtering caused by impacting ions, atoms, and molecules will also contribute to changing the condition of the satellite's surface.

Calculations substantiate the generally accepted opinion that sputtering erosion will probably never cause a structural failure of a space vehicle. It is entirely possible, however, for enough damage to be done to the vehicle's surface that its emissivity and absorptivity characteristics will be changed sufficiently to disturb the temperature control, and ultimately cause thermal damage.

Sputtering of the surface of a satellite largely depends upon the parameter causing drag. Except in the low atmosphere, the charged particle drag is comparable to the neutral drag on an object.

As a vehicle travels through an ionized medium, the surface assumes a negative potential because thermal velocities of the electrons are over 50 times greater than the velocities of the ions, hence the electron flux is greater than the ion flux. Although this tends to be counteracted by the photoelectric effect on the day side, its magnitude is not believed sufficient to overcome the charge due to the collection of electrons on the night side. Thus, a net negative charge will result.

It was calculated that a vehicle could obtain a potential of several thousand volts during each pass through the Van Allen zones. The calculation is in doubt, however, since it is based on an assumed energy distribution of electrons greater than is shown by recent measurements. However, if these potentials occur, they would in turn cause an increase in the effective radius of the vehicle by a factor of 10, and in the effective cross-sectional area by a factor of 100. In the case of Vanguard I, the pass through the inner radiation belt resulted in a two-fold increase in the mean drag.

The drag on a satellite is also dependent on particles resulting from solar flares. From correlations of orbital data, and radio wave charts of the sun, it appears that particles reaching the Earth about 24 hours after a solar flare, cause an increase in the charge on the satellite, thus increasing the effective cross-sectional area and hence increasing the drag.

It should be noted that at sufficiently high altitudes the pressure of solar radiation acting upon a vehicle may be equal to or greater than the atmospheric drag. This was evidenced in the case of Echo I.

In addition to thermal effects already mentioned, a satellite will experience an erosion process called sputtering, due to the bombardment of the surface by particles of reasonably high energy. The amount of sputtering that occurs depends on number and energies of the particles.

Bombarding ions gain additional energy due to the charging of the vehicle. Prior to the discovery of the Van Allen belts, the vehicle charge was thought to be 10 to 60 v. However, revised calculations indicate that a vehicle could reach a potential as high as 1000 v. Although it is true that such a potential would be maintained only while passing through regions with large numbers of high-energy particles. The 1000-volt value must be considered in estimating the amount of sputtering.

Calculations of sputtering have been based on the assumption that the particles strike the surface at normal incidence. Recently quantitative data have been obtained indicating that impact at oblique angle of incidence can increase the sputtering rate as much as 16 times that which would occur at the normal angles of incidence. There is considerable speculation about the values of the threshold energy for sputtering. Until recently the accepted values were in the range of 30 to 100 ev. However, recent experimental work indicates that sputtering occurs for energies as low as 5 to 10 ev. According to these measurements, impacts having the energies associated with orbital velocities should be expected to produce erosion due to sputtering. The exact quantitative effects cannot be predicted at this time because of insufficient data.

Although it is not likely that vehicles will be flown continuously at altitudes as low as 120 km, the amount of material sputtered during their periodic trips through low altitudes will be significant. Moreover, there may be other areas where the sputtering rate is greater than anticipated.

Meteorites

Studies of the nature and number of small aggregate particles in interplanetary space preceded the era of rockets and satellites. Visual and radio meteor-observation, measurements of solar light-scattering, zodiacal light, and other techniques, as well as examination of meteoritic specimens which reached the earth's surface, provided fairly accurate information on the influx rate and velocities of particles larger than 1 cm.

Meteor observations established that the maximum heliocentric velocities of most particles is less than 42 km/sec at the earth's distance from the sun, and that meteoritic particles travel in orbits which are randomly distributed with respect to the plane of the earth's orbit. The size, mass, and densities remained uncertain.

Although recent direct measurements have been made from rockets and satellites, the sampling area and time available are small compared to that available to meteor observers. For example, if the entire surface of a satellite could be used as a measuring area for one year, the total exposed area-time integral would be on the order of $10^7 \text{ m}^2/\text{sec}$, while from the ground $10^9 \text{ m}^2/\text{sec}$ of sky can be observed in one second. It is also difficult with rocket and satellite measurements to determine the particle size from the interaction with the detecting unit. Present methods allow instrument calibrations for velocities up to 7 km/sec, whereas actual impact velocities must range from 11 to 70 km/sec.

Considering all the uncertainties, estimates obtained by various investigators are in fair agreement with the few direct measurements available. For example, for particles of 10^{-8} grams, the fluxes measured by Explorer VI and Vanguard III were 10^{-5} particles/ cm^2/sec and 10^{-3} particles/ cm^2/sec respectively. Whipple's estimated value for particles of this mass was 10^{-4} . Similarly, for particles of approximately 3×10^{-10} grams, Explorer VI and Midas II measurements are 10^{-4} and 10^{-2} respectively, whereas Whipple's estimate was 10^{-3} particles/ cm^2/sec .

STRUCTURAL MATERIALS

B. Chasman

Directorate of Materials and Processes, ASD

The weapon systems of the future represent both the cause and the effect of structural materials research efforts. On one hand, we must obtain the improved materials capability required for these systems, and on the other hand, the feasibility of solving the materials problems in some manner, as indicated by our research efforts, to provide the basis for presenting these increased capabilities with some expectation of attainment.

Thus, in this broad scope, we are concerned with two questions:

- a. The changing requirements for structural materials associated with future systems
- b. The potential of structural materials for meeting these needs.

At this point we must define "structural materials" so that the broader aspect of this discussion may be kept in mind. Structural materials are those which provide the physical embodiment of the component, device, or vehicle, and which carry the loads or maintain the juxtaposition of the component parts. We include materials for wing structures carrying aerodynamic loads, materials for structures that contain or resist the forces of propulsion, or power, materials used to maintain the shape or orientation of the solar collector, the radiator, or the avionic component. The diversity of application of our advanced structural materials validates this definition.

It is apparent that our first question—the changing needs for structural materials—is essentially, how is the sum total of future vehicles and subsystems, performance, characteristics and configuration, different from that which has been done before—as translated into materials terms? Although the first part of the question is difficult, it is straightforward and directly amenable to analysis. The second part, the translation, is most complex because it involves the process of design.

Although the designer molds his article from material, his probable selection and demand on material reflects the compromise of many forces, type and magnitude of loads, volume to be enclosed, minimum weight, temperature and other environmental factors, as well as fabricability, producibility, reparability, cost, etc. Thus exact materials selections for specific structural needs are inextricably intermixed in the compromises of design. This aspect is in itself the subject of a separate presentation. Nevertheless, careful examination of the demands on the designer and his response in past and present problems, we can, and do translate these future systems into requirement trends for structural materials.

Environment, natural and induced, is one of the main factors in design and material selection. It is a useful parameter in the examination and summation of future system requirements. The induced environment reflects the trajectory or path as well as the shape of the vehicle, and the particular requirements for propulsion, power, and avionic subsystems.

With this in mind, we can visualize all aerospace missions divided into three major categories:

1. Suborbital—where we are interested in attaining hypersonic velocities that will permit the penetration of regions up to the lower fringe of space, with potentially rapid return through a carefully prescribed path.
2. Orbital—where we desire to establish our payload as a more or less permanent satellite for a specific mission.
3. Extraborbital—in which we desire to locate in the cislunar, lunar or interplanetary space.

Materials problems are common to all three categories, nevertheless each represents a significant difference in natural and induced environments.

In the sub orbital category, we can launch our vehicle vertically and bring it back through a ballistic trajectory, as for example Atlas, with great speed, for weapon delivery. Or we can build a high drag, smoothly decelerating body which may be manned. We can launch our vehicle horizontally, and bring it back in an aerodynamic trajectory as we now do with the X-15. By the use of aerodynamic lift, we reduce propulsion requirements, gain longer flight time and greater maneuverability.

Consider the next category: an orbital vehicle with a longer duration, useful mission, (figure 2) we still use 2 types of exit trajectories—horizontal with aerodynamic lift, or the brute force vertical take-off, in which the thrust would have to support and exceed vehicle weight. This puts our intrepid adventurer on the orbital highway, looking at the scenery and maybe dodging the traffic. It could also be the way station for a longer range mission, to provide refueling, changing the guard, or transfer of equipment, of a subsidiary vehicle, entering matching orbit in a similar manner, and would have several choices of returning to Earth. This re-entry could be a rapid, hot ballistic one, decelerated in the last minutes in the atmosphere for soft landing, or an aerodynamic maneuverable re-entry to a specific landing field. The specific path chosen would be determined by the ability of the payload to withstand the duration and amount of deceleration, and the ability of the vehicle structure and material to resist the induced environment.

We may consider single or multiple steps to accumulate the extra orbital velocity (figure 3). We could use vertical or horizontal aerodynamic take-off to orbital velocity and then accelerate to extra orbital velocities with optimum propulsion method and trajectory to suit the mission. As indicated previously, we could start our extra orbital mission from an existing way station satellite, or even a handy piece of real estate only 238,000 miles away from us. The extra orbital mission requires the greatest accumulation of energy and potentially the longest exposure to galactic environment.

In each category, we are interested in progressively increased payload capacity, increased versatility and effectiveness of military operation, and lower cost. This connotes such other considerations as reliability, durability, and maintainability.

We can now deduce by inspection that all of our systems will be concerned with the natural environment, and that the extent and duration of penetration of the reaches of aerospace reflect increasing concern with the behavior of structural materials in the less familiar environment.

However, further analysis reveals two more important problems derived from the induced environments:

1. light weight construction
2. extreme temperature resistance

In our analysis we will also see that in many cases, the problems are concurrent, and assume progressively increasing importance in future military weapon systems. Airborne vehicles favor lightweight construction; other things being equal, the lighter the better. The less dead weight we haul aloft the greater the payload. In the aerodynamic lift machine, the conventional aeroplane, the propulsion force needed to overcome drag and deliver payload is only a fraction of the total lift produced. For long range, fuel may be 50 percent of the gross weight, and structure may be 25 to 30 percent, (figure 4). In the vertical lift, propulsion force directly produces lift capacity and overcomes the drag involved in delivering the payload. For sub orbital devices, fuel is 85 percent or more of gross weight and the remaining 15 percent covers payload, which includes structures, guidance and control equipment. Increasing the velocity requirement to orbital and extra orbital values increases the energy requirements by the familiar velocity squared relationship, and therefore the fuel requirements. So, for the expanding scope and payload of future military operation and concurrent with tremendous efforts to increase the efficiency of our propulsion systems, we can see demands for more and more fuel per pound of payload and less and less pounds available for structure.

The temperature problem in our vehicle is closely associated with the projected mission. The great source of heat input to the vehicle occurs during passage through the atmosphere at very high speed, and in the generation of the original thrust.

We remember the shape of the aerodynamic heating curve which indicates the temperatures experienced with increasing vehicle velocity (figure 5). Moving at 3 to 4 times the speed of sound, some areas will be exposed to temperatures of 500 to 1200°F. In the lower altitudes, for this operating regime, propulsion is usually provided by airbreathing engines. Using fossil fuels, the propulsion agglomeration of structural materials encounters temperatures of about 3000°F in the combustion process, and extracting energy from the gas stream at somewhat over 2000°F, under severe vibratory and steady loading.

Velocities to Mach 5 and higher expose vehicle areas to temperatures in the range of 1500° to 2000°F. Concurrently our propulsion system needs higher energy fuels, and process temperatures enter the 3000° to 5500°F range. In addition, we introduce problems of containment of quantities of low density cryogenic fuel requiring relatively large volume containers with insulation to control heat flow into the liquid. If an exotic fuel is used, the increased volume and insulation problem may be traded for compatibility problems. Here we have increased the propulsion energy required, increased the volume contained, both increased and decreased from prior norms the temperature and temperature gradients. Concurrent normally desired increase in range, fuel, and payload, increases burden on the structure.

Let us examine the orbital and extraorbital regimes. Both imply attainment of operating velocities beyond the upper end of our velocity curve. Depending on the velocity, (attitude route used to exit, to orbit, or beyond) our induced environmental temperature may range up to about 2000°F. In this operating regime, we anticipate propulsion systems that will integrate the features of the airbreathing rocket, and possibly nuclear and electric devices, with high energy and exotic propellants, which will involve process temperatures as high as 8000°F; problems of compatibility of materials with propellant, exhaust, and internal and external environment will be multiplied.

The desire to increase payloads, and the greater energy needed to attain the desired velocities, can only result in added demands on the designer to reduce the structural weight fraction, which will consequently make greater demands on structural materials.

The job of absorbing or dissipating energy during re-entry deceleration of orbital and extra orbital vehicles, is another facet of the induced environment problem. The path that we chose for re-entry has strong influence on the induced environment, the vehicle configuration and the magnitude of the temperature problem. The quickest return with the greatest deceleration is the ballistic type path which results in the highest peak heat flux. Since the duration is short, the total heat accumulated will be less than for other re-entry paths. Typical heat flux, and temperature levels are shown in figure 6. In cases where more moderate decelerations are required for manned vehicles in which increased maneuverability and fly-back are desired, lifting bodies, figure 7, or glider shapes, figure 8, are used.

The lifting body must operate at fairly high velocity to sustain itself in a controlled path, and enters at a fairly rapid rate in relatively short time. The addition of the "wing" gives increased aerodynamic lift, allows slower re-entry velocities and requires longer re-entry time. For the glider, the peak heat pulse may be lowest, but because of the long time period, accumulates the greatest total heat. Typical values are shown in figure 9, together with representative design configurations.

We must consider at this point that the examination of other subsystems indicate similar concern with light weight construction and extreme temperatures. Thus, high levels of flight vehicle power with more kilowatt output per pound weight for increasingly longer periods of reliable operation, results in higher operating temperatures and structural loading, together with problems of containing the reactive energy transfer fluids.

Our efforts thus have been to indicate the changing and increasingly severe requirements for structural materials in future systems. Before we throw up our hands in despair, let me say that changes in design techniques and significant improvements over a period of time in the capability of structural materials are providing initial solutions to these problems. Nevertheless, we will examine our capability for using present materials to solve these problems. And now, the second problem, the potential of structural materials for meeting the need.

As indicated, the selection of structural material is inextricably intermixed in the compromises of design. It is well nigh impossible to identify one overriding parameter that controls design selection. Strength, weight, and temperature are important factors, therefore these have been used to convey the general capabilities of materials, for comparison with the trends of potential needs.

In this formula chart, figure 10, of tensile strength to weight ratio vs. temperature, we see no overriding trend toward high strength with temperature. Quite the contrary is true. We find that as temperature increases, attention moves from aluminum and magnesium, overshadowed by the tremendous potential of filaments, beryllium and titanium, chrome nickel steels, super alloys, refractory metals and graphite material. Beyond 3000°F we are limited to graphite, tungsten, ceramics, and other still not defined combinations of squares in the periodic table. All manner of combinations of the materials shown may be contemplated also, if optimization of a specific performance parameter is desired.

The trend indicated is significant in another aspect—the increasing difficulty to form and fabricate special environmental protection needs, leading up to the designers nightmare—the brittle materials and the loss of the cushion of ductility.

The contribution of present materials to the solution of our problems, is as follows:

1. There are materials that offer some load carrying ability at high temperature with low strength to weight ratio.
2. There are materials that can sustain exposure to very high temperatures.
3. There are no structural materials that can withstand the very highest temperatures projected.
4. We must look to design alternatives in the use of materials wherever possible, to obtain the future light weight structures.

Where temperature is not a significant problem and our emphasis is on light weight structures, we have many materials and design techniques available. For some of our applications with extreme emphasis on light structure, the inflatable expandable materials may be the answer, figure 11. In outer space, gravity and air density are greatly reduced, and also weight and drag effects. So, we have less need for heavy construction. All that may be needed in our space structure is sufficient strength to hang together in spite of the minor induced loads from equipment operation of crew movements. Thus, for permanent type satellites, way stations, or moon lodges, we can consider some sort of foldable, suitably coated, fabric bag. Lofted into orbit by a booster, it would inflate itself for an active function, possibly carrying only electronic equipment. It may be one of several similar packages to be assembled into something more complex on the site. There are several variants that are being explored in terms of materials for inflatable structures, depending on the function that the structure is expected to carry out. There is the simple, inflatable balloon, such as the Echo experiment, or a functionally configured structure of double wall construction inflated with air, a gas, or a cellular material. We visualize that once in orbit the foaming process to obtain the cellular material would both produce the inflation as well as permanently rigidize the structure.

Configuring materials that could be collapsed, and subsequently expanded to the desired shape, and honeycomb panels are also a possibility. When we refer to fabric, we include: cotton, rayon, nylon, etc.; as well as filaments, or even very fine metallic wire of high strength steel or superalloys, as well as new inorganic fibers such as graphite and metallic oxides.

Alumina, silica, beryllia, zirconia, choria, essentially single crystal fibers, and so we have a potential solution to the requirement for a low strength exceedingly light weight structure, with resistance to increasing temperature levels.

Where load bearing is an important factor, and local temperatures are getting uncomfortably high, we compare the brute force approach using the higher temperature material with other approaches, such as local cooling with ambient air, (this has been done in subsonic aircraft nacelles) or with air or fuel in an active cooling arrangement in air-breathing and rocket engines. Passive cooling arrangements of ceramic insulative coatings may be used to retard heat flow and protect against oxidation.

As the problem becomes more acute in higher heat flux, limited space, materials compatibility duration, and durability, the solution will be that one which results in the least

compromise to the weapon system. Where varying degrees of active and passive cooling are considered in conjunction with varied levels of operating temperature, a complex design evolves.

A small amount of cooling may reduce the operating temperature to the point that a new material selection can offer a significant increase in operating stress level. Of course, the effect of the permanent weight of the cooling arrangement must not offset the benefits obtained by operating the new material at a higher stress level. For short durations and modest heating conditions, the materials may be able to absorb the heat input with only a moderate temperature. The extreme of this approach of course involves selecting material specifically for its high specific heat, and hopefully at the same time use it as a structural element.

As the temperature and duration of exposure of structure increases, the alternative is to permit modest increases of structure temperature level. Under severe conditions it may be necessary to operate prime structure at relatively high temperatures 1500 °F and also isolate this structure from the peak heat input with insulations. This also requires that all components, ducts, wiring, controls, etc., in the prime structure area must also operate at this high temperature. Design decisions must also consider the effect of this situation on the overall weapon system. For the short duration peak heating conditions non-reusable ablation cooling has proved very successful, maintaining the prime structure at modest temperatures.

In any case, there will be a very definite and unavoidable price paid for the privilege of operating in these increasingly severe natural and induced environments. Therefore continued pressure will be placed on the researcher to find improved materials. We sense the designer's hope for multipurpose materials—load bearing insulation. There is increasing recognition that ingenious solutions will come from a closer partnership of designers and materials people, gained by the knowledge and experience from all other technologies.

Certainly for the most severe requirements for load bearing and temperature resistance, the designer will have to use ceramics; this multipurpose material, he will use with some design limitations, no doubt. The timing of this occurrence will be influenced by the importance of the need, the alternatives available, and the confidence in the materials developed by thorough knowledge of the capabilities and limitations of the materials that must be used. It thus rests with our materials community to provide the ultimate capability for our future weapon systems.

SUB ORBITAL

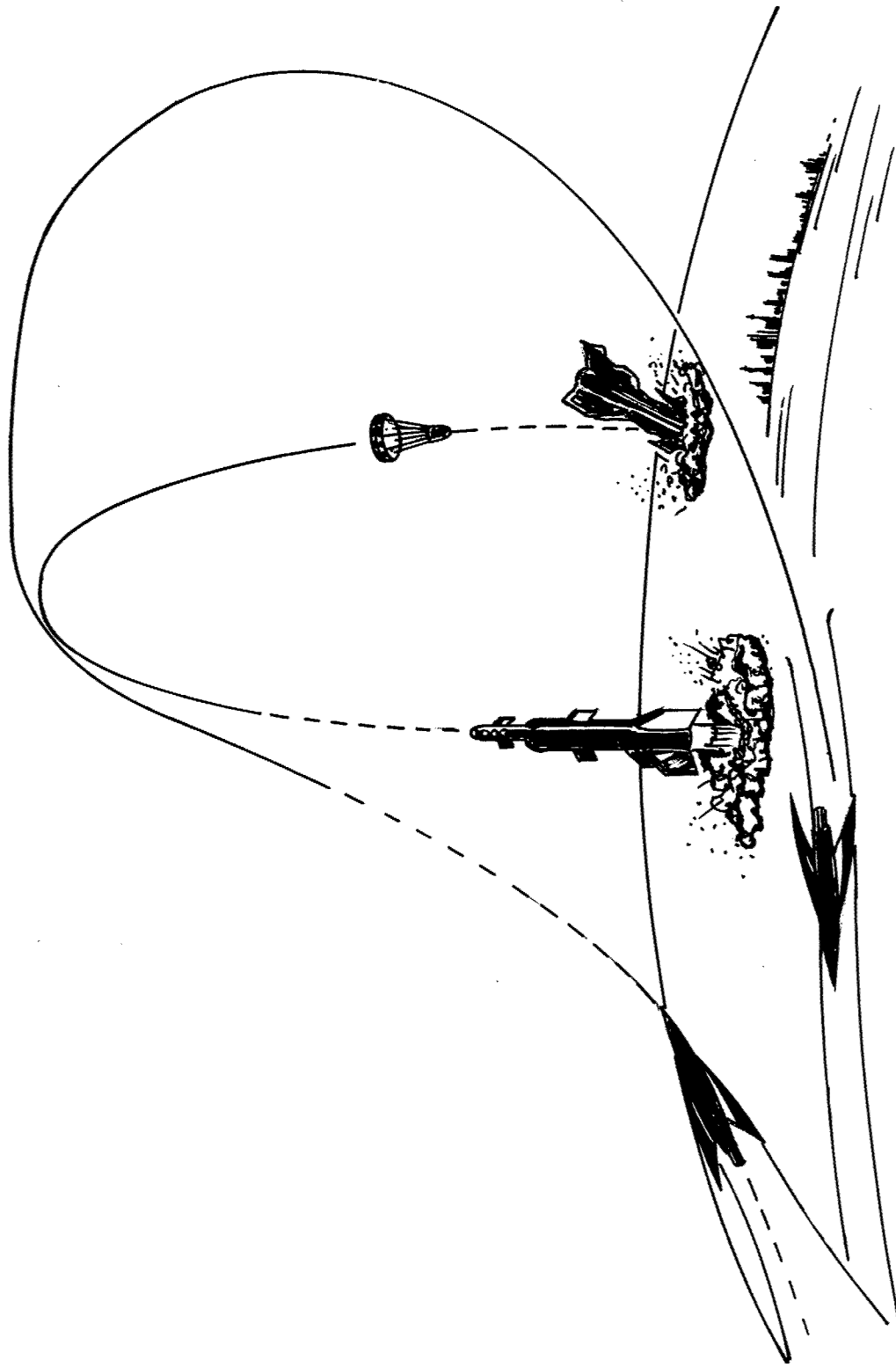


Figure 1.

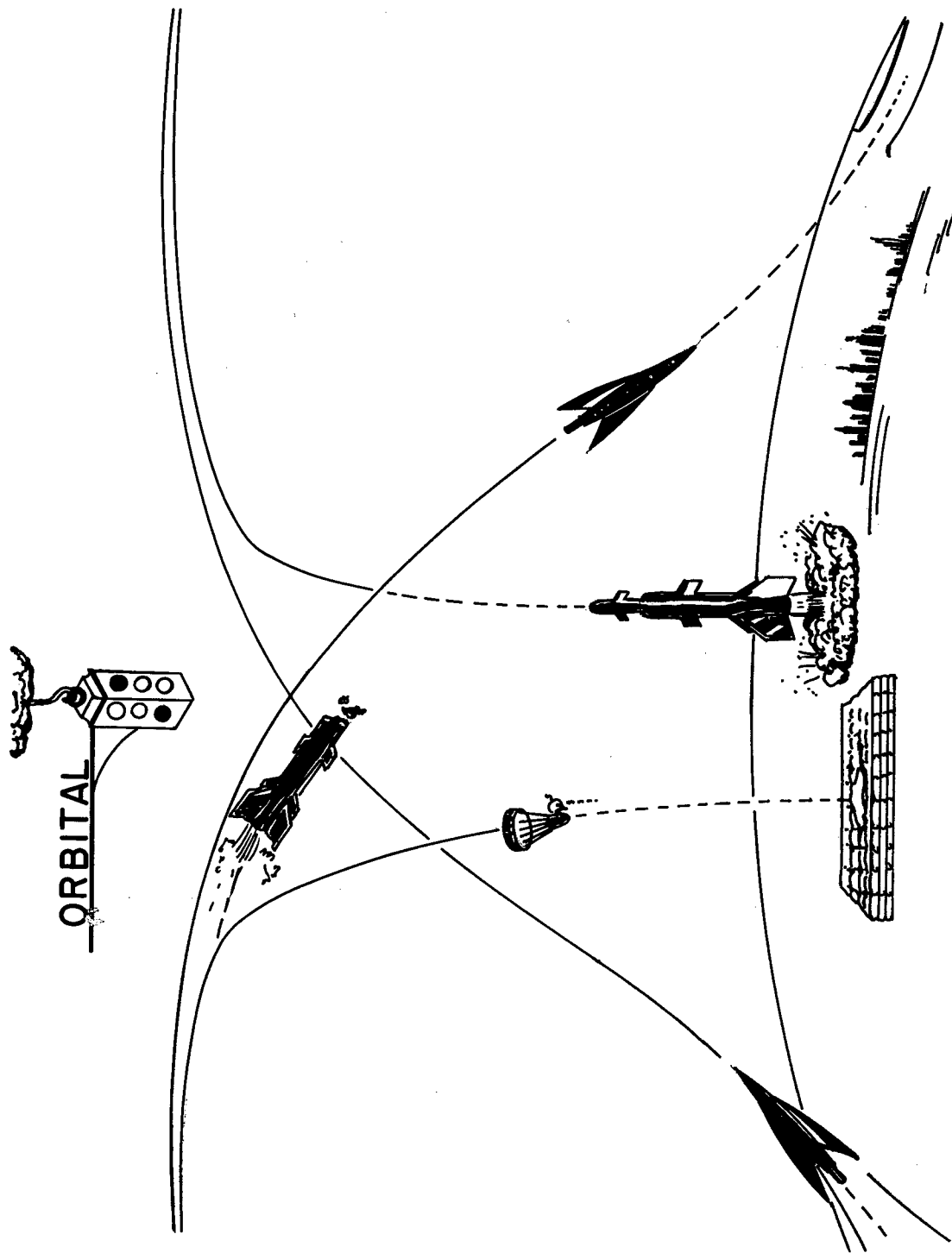


Figure 2.

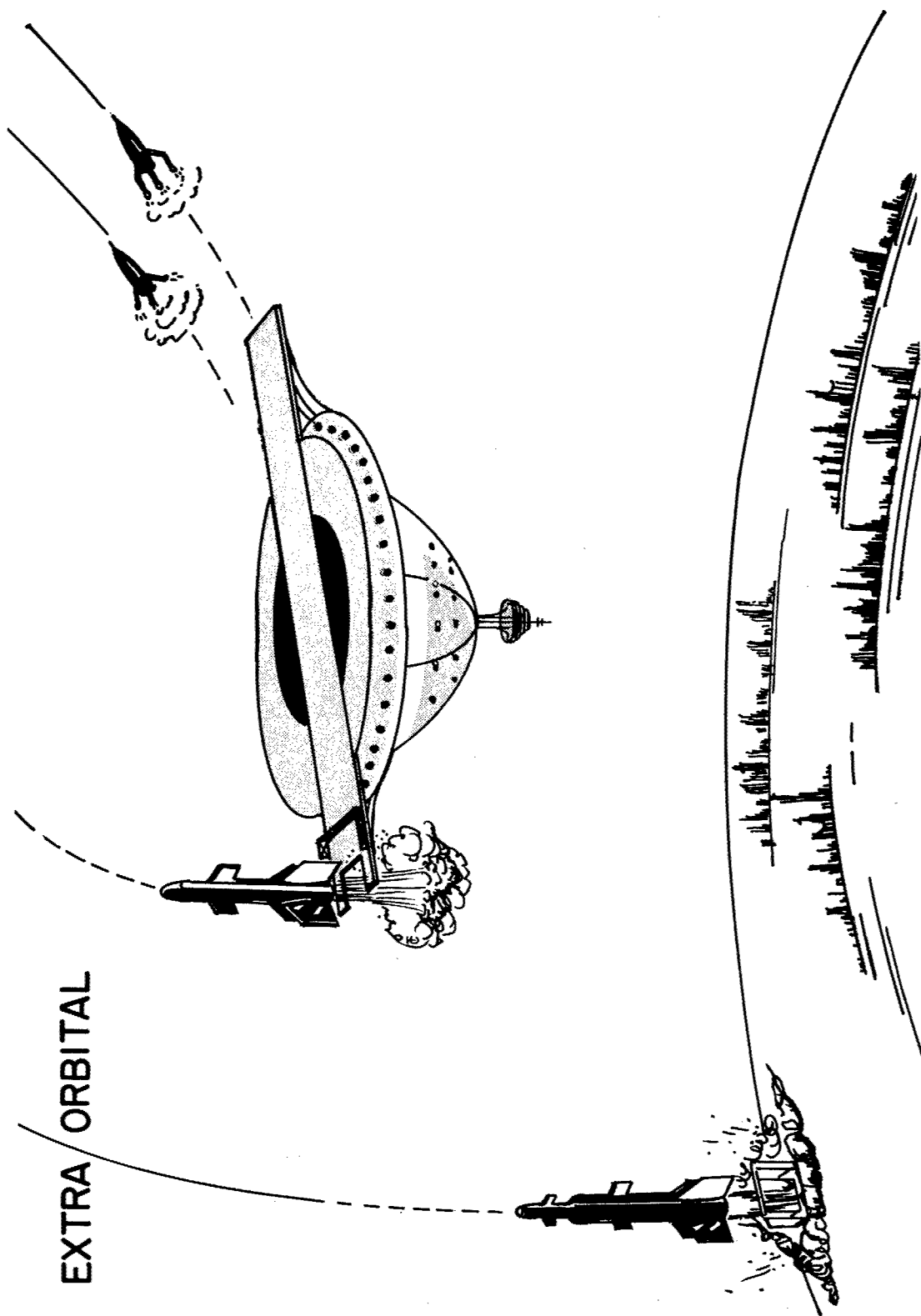


Figure 3.

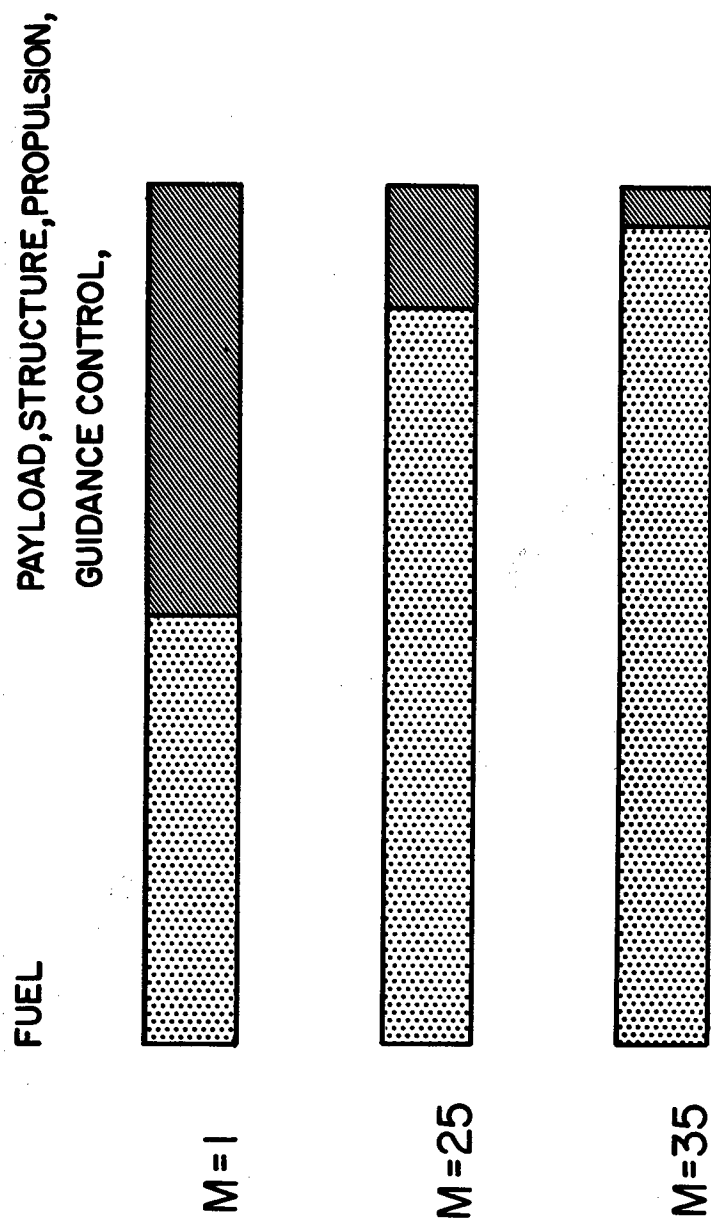


Figure 4.

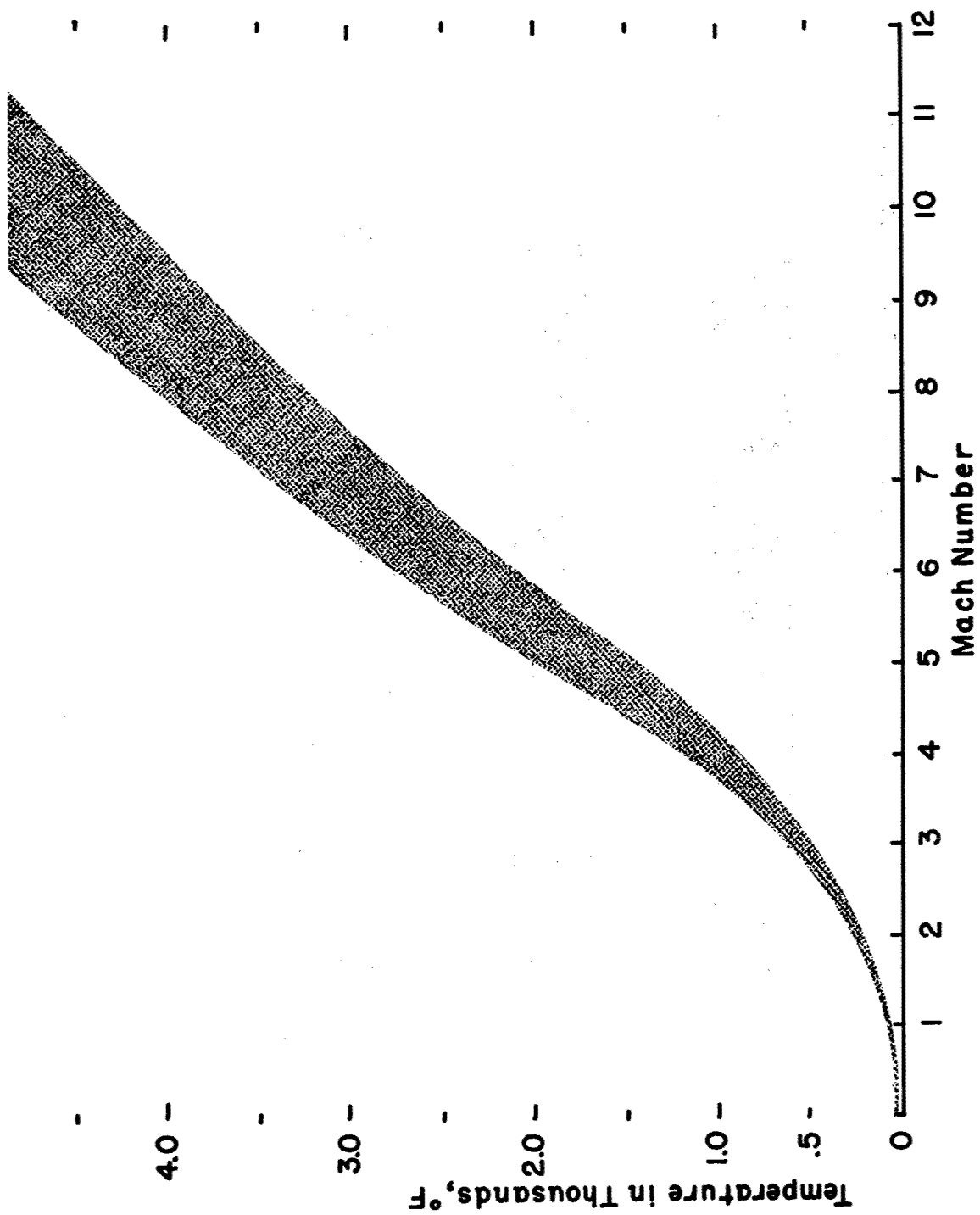
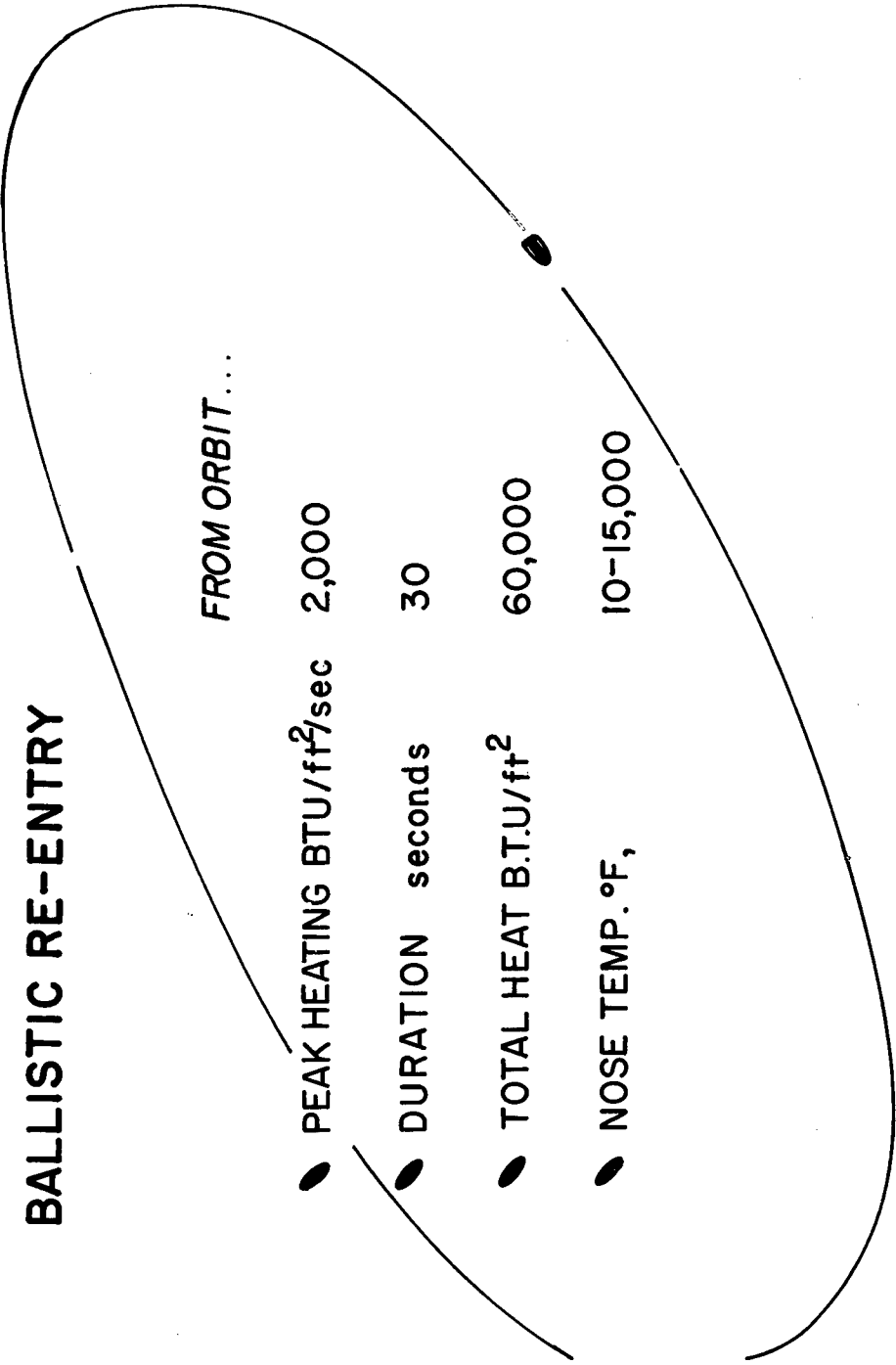


Figure 5.

BALLISTIC RE-ENTRY

FROM ORBIT...



● PEAK HEATING BTU/ft ² /sec	2,000
● DURATION seconds	30
● TOTAL HEAT B.T.U./ft ²	60,000
● NOSE TEMP. °F,	10-15,000

Figure 6.

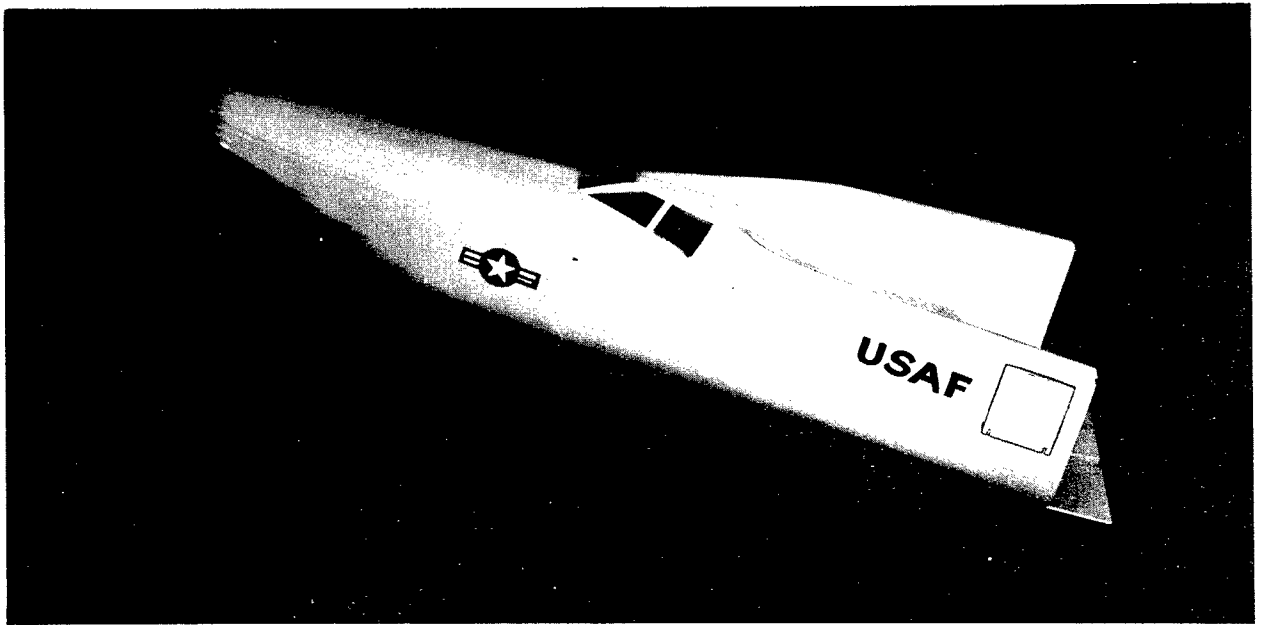


Figure 7.

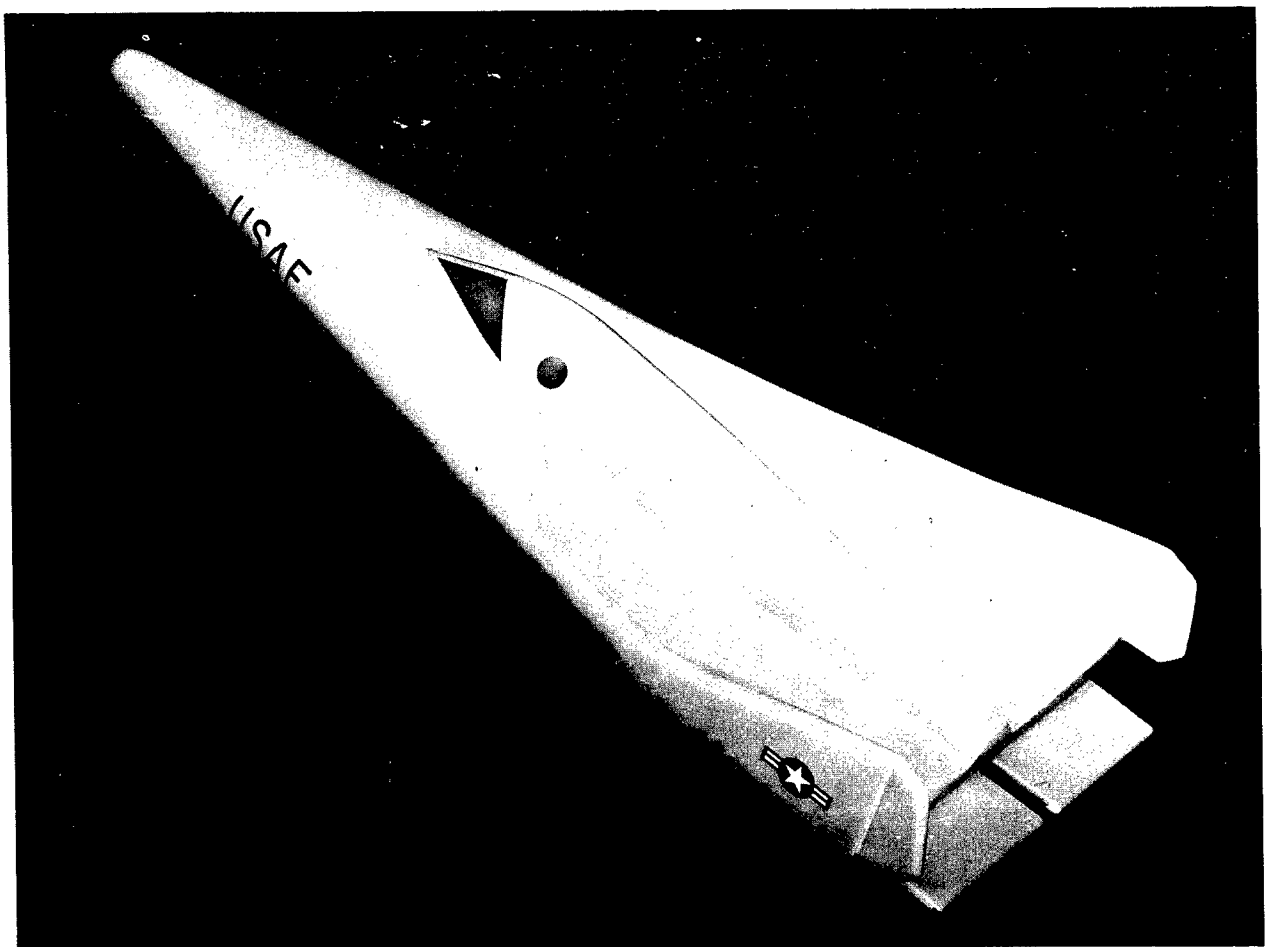


Figure 8.

MANNED RE-ENTRY ***From ORBIT***

	Lifting Body 1/d1.5	Glider 1/d2.0
PEAK HEATING B.T.U./ft ² /sec.	150-175	100-140
DURATION seconds	720	1200
TOTAL HEAT B.T.U./ft ²	110,000	150,000
NOSE TEMP. °F,	4,000	3,600-4,000
LEADING EDGE °F,	-	2,700-3,000
BOTTOM SURFACE °F,	2,300-2,700	1,000-2,000

Figure 9.

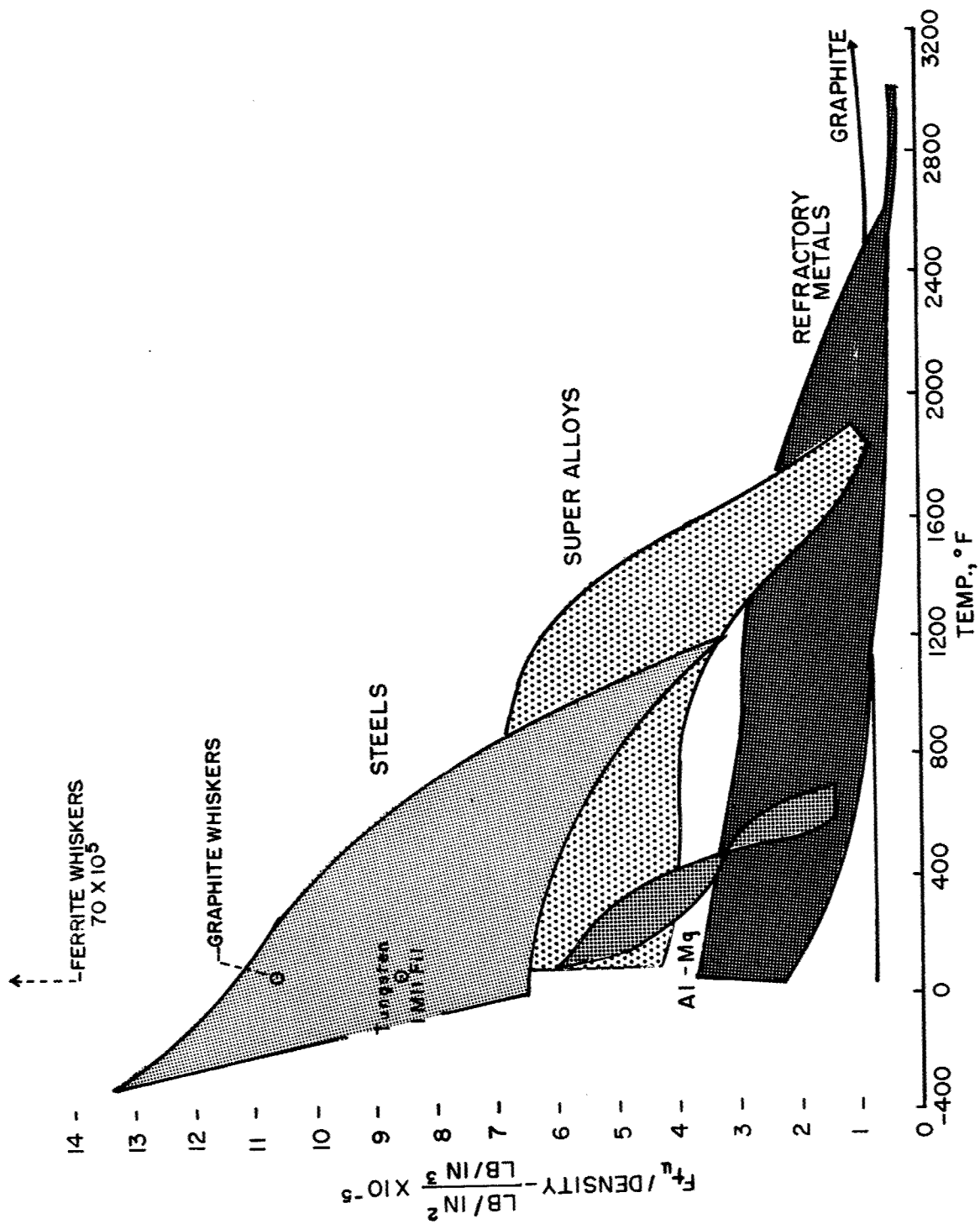


Figure 10.

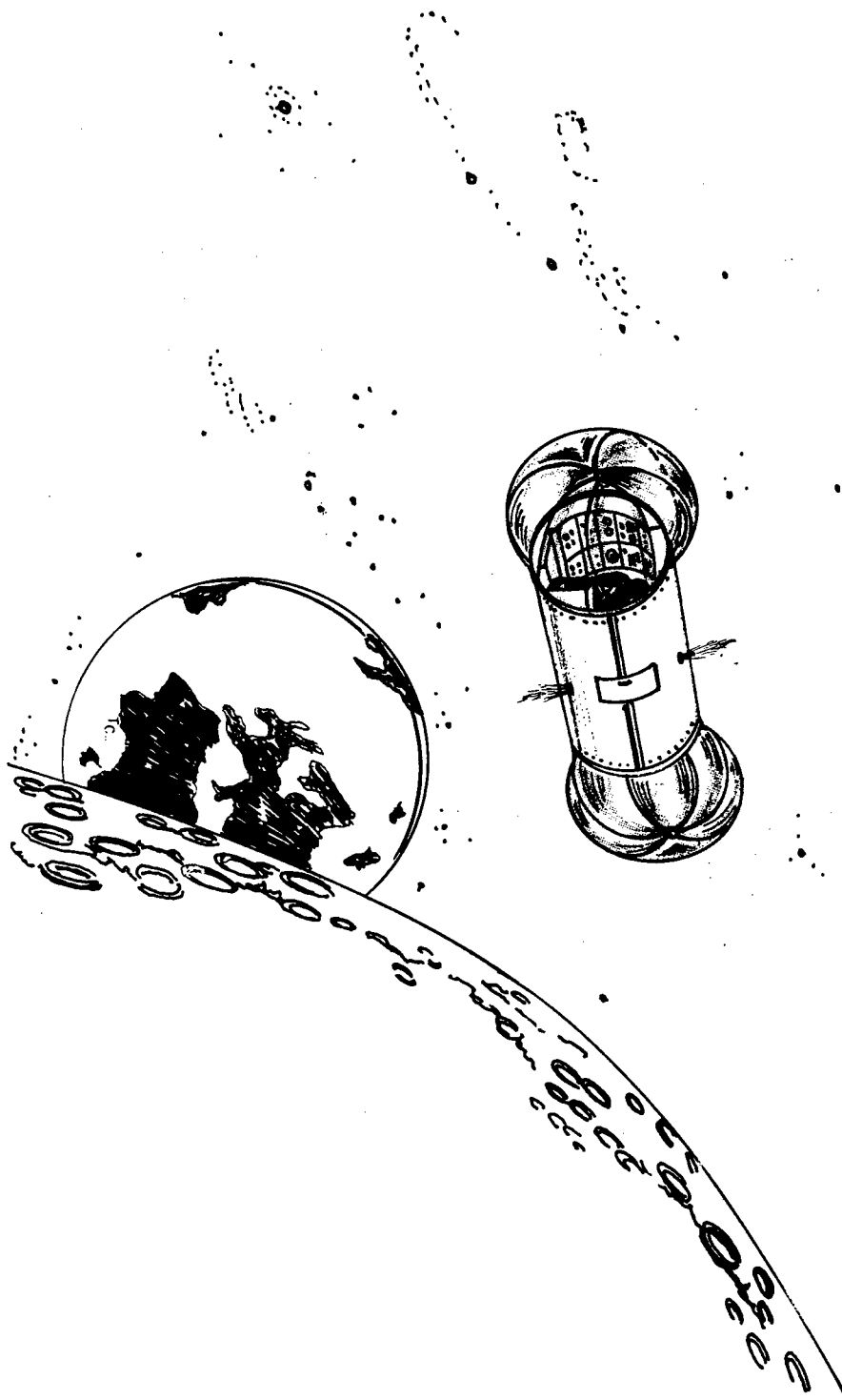


Figure 11.

STRUCTURAL METALS TO 1800°F

Chairman	Lt. Col. E.M. Kennedy
Speaker	Captain L.F. Bubba
Speaker	Mr. P.L. Hendricks
Panel Members	Mr. H. Middendorp
	Mr. B. Cohen
	Mr. E. Horne
	Mr. H. Zoeller
	Mr. I. Perlmutter

A NEW LOOK AT SUPERALLOYS

Capt. Lawrence F. Bubba

Directorate of Materials and Processes, ASD

The past history of superalloy development indicates that perhaps the title would be more appropriate as "Another Look at Superalloys." Each time it was felt that everything worthwhile had been accomplished, major new improvements came about to rejuvenate interest in superalloys. In 1945 maximum operating temperature at high engineering stress levels was 1550°F, in 1950 the limit rose to 1700°F, today 1800°F, and the maximum limit has not yet been reached. Credit must be given to industrial organizations for most of the latest improvements in superalloys, since almost all Government supported research was dropped about 1954. Most of the improvements in composition and mechanical properties have been achieved by improved melting, casting, and fabrication techniques.

The very definition of "Superalloy", "an alloy developed to withstand relatively high stresses at high temperatures, a condition wherein good oxidation resistance is frequently required", reveals their applicability in the space program. These alloys were initially developed for aircraft gas turbine components operating in the range 1200-1300°F, and today the evolution of superalloys permits satisfactory service with blade temperatures at 1750°F. Many of the alloys have been adapted for production in sheet form for structural and skin applications. Wrought superalloys have also been developed specifically for sheet-metal applications; a prime example familiar to most of us is the use of Inconel X as the skin material for the X-15 rocket plane.

The superalloys are divided into three groups: (1) Nickel-base; (2) Cobalt-base; and (3) Iron-nickel-chromium-base alloys. They are particularly applicable in the temperature range 1200-1800°F, where they excel in strength-to-weight ratio and oxidation resistance, both characteristics considered to be of prime importance for space application. These alloys have become available in the wide variety of forms necessary to fulfill the needs of structural components for missiles and space vehicles for relatively short time application, and ramjet engine components such as turbine wheels and blades or fuel elements for reactors. The latter uses place emphasis on long time properties such as good creep, stress-rupture, and oxidation resistance for continuous or intermittent operation at high temperatures and relatively high stresses. Figure 1 demonstrates quite vividly the role of superalloys in the temperature range 1200-1800°F. The superalloy band includes wrought and cast alloys, with the wrought alloys (top part of the band) having higher strengths initially but not enjoying as much stability at elevated temperatures. Wrought alloy strength begins to drop around 1200°F, whereas cast alloy strength (lower part of the band) is maintained close to 1400°F.

Nickel-Base Alloys

Nickel-base alloys have evolved from the simple Nichrome V (80 Ni-20 Cr) alloys to the complex precipitation-hardening present day alloys. Table 1 illustrates the changes in chemical composition achieved through alloy development and these can be correlated with improvements in mechanical properties.

The Nimonic Alloys have been developed by the British in response to increased needs for gas turbine engines. "Nimonic 80" was developed in 1940 and "Nimonic 105" in 1958. "Nimonic 80" introduced precipitation-hardening nickel-base superalloys. Research and development in the United States paralleled the British work on superalloys with "Inconel X", basically the same as "Nimonic 80", and the complex superalloys such as Waspaloy, Unitemp 1753, the Udimets, Astroloy, and the high strength casting alloys such as Haynes Alloy 713C, Nicrotung, and IN-100 have been the most recently developed.

The changes in chemical composition during the development of these alloys involved the addition of cobalt, aluminum and titanium, and shifting the ratio of these two, refractory elements (Mo, W, Ta, etc.), and minor additions of boron and zirconium.

The nickel-base superalloys are strengthened by three different mechanisms: (1) solid solution hardening; (2) precipitation hardening; and (3) the effects of boron and zirconium additions. Chromium contributes to the excellent oxidation resistance of these alloys, raises the recrystallization temperature, and strengthens nickel by solid solution hardening. Aluminum and titanium strengthen the matrix material by precipitation of the gamma prime (γ'), $\text{Ni}_3(\text{Al, Ti})$ complex. Increasing the aluminum also gives the added benefits of decreasing the density and contributing to the excellent oxidation resistance. Cobalt increases the solvus temperature, thereby permitting retention of the precipitate out of solution to a higher temperature, and also increases the solubility of carbides in the matrix. Refractory metal additions contribute to solid solution strengthening and carbide formation, and thereby improve the creep-rupture properties of superalloys. The addition of limited amounts of boron and zirconium improve the stress-rupture properties of these alloys. Excessive amounts of these elements have proven to be detrimental in that a brittle network forms in the grain boundaries. Boron is more effective than zirconium and a combination of both has proven to be most beneficial. These alloying elements retard the effects of carbide and γ' precipitate agglomeration at the grain boundaries from late in the initial stage of creep until the start of the third stage. Boron and zirconium atoms are believed to occupy voids in the grain boundaries and impede dislocation movement. The overall effect is an increase in rupture life and ductility.

Figure 2 illustrates the effect of temperature on the short time tensile strength of wrought and cast nickel-base superalloys. The curves support the previous discussion of the strength/weight plot with respect to strength-temperature stability of cast vs. wrought products. The mechanical properties can be correlated with the above discussion on composition. The highest strength wrought alloys from room temperature to approximately 1100°F are Udimet 700, Unitemp 1753, Astroloy, Udimet 500, and Rene 41 in approximate order. At about 1200°F the order changes slightly showing Astroloy and Udimet 500 to be slightly superior and at elevated temperatures (1800°F) the strengths of all alloys have dropped approximately 100,000 psi with Astroloy displaying some superiority over Udimet 700. Inconel X has been included to show the improvement that has been achieved in recently developed alloys.

Much the same condition exists in the cast alloys. The most recently developed IN-100 and NASA TN-D-260 demonstrate superior strength properties to Inco 717C, Nicrotung, Inconel 713C, and Udimet 700 at elevated temperatures (1800°F). The drop in strength of the cast alloys does not occur until approximately 1400°F as compared to 1200°F for the wrought alloys. Cast alloys also remain slightly stronger between 1600-1800°F.

A review of table 1 reveals that the higher strength wrought alloys contain 15-20 Cr, 6-20 Co, 2.5-8 (Al + Ti) in varying ratios, one or more refractory elements, .003-.1 B, .02-.1 Zr, and 1-11 Fe. The complexity of these alloys introduces several of the strengthening mechanisms discussed previously and is responsible for their high temperature strength. On the basis of chemical composition, it sometimes becomes difficult to distinguish between cast and wrought alloys; however, the cast alloys are lower in chromium, generally considerably lower in cobalt, and higher in aluminum + titanium with the ratio in favor of aluminum. They also generally contain more than one refractory alloying addition (Mo, W, Nb, V, Ta). These alloys are usually used as cast, whereas a variety of heat-treating cycles have been established to impart the specific characteristics desired for service of the wrought alloys.

Cobalt-Base Alloys

Unfortunately, cobalt-base superalloys have not been developed at a rate comparable to the nickel-base alloys. A partial explanation for this may be the lack of Government support and the limited availability of research and development funds in industry. The cobalt-base superalloys developed initially for application as precision cast gas turbine blades have demonstrated excellent creep and rupture properties and good oxidation resistance up to 2000°F. Consequently, these alloys have found application in high-temperature gas engine wheels and blades, turbo superchargers, and power plant equipment.

Cobalt-base alloys contain an appreciable amount of chromium (18-20 Cr) and carbon (0.2-0.6 C), and derive their strength chiefly through the precipitation of chromium-carbide. However, the presence of refractory metals such as tungsten, columbium, and molybdenum also contribute to their strength through solid solution hardening. Nickel is employed primarily to stabilize the high temperature crystallographic structure (FCC) form of cobalt. Table 2 gives the composition of some more recently developed cobalt-base superalloys and HS-25 (L-605) and Stellite 31, two earlier alloys. The addition of boron has been found to improve the elevated temperature mechanical properties of the cast alloys, and titanium additions to wrought alloys have improved high temperature strength.

Figure 3 illustrates the effect of temperature on the strength of cobalt-base superalloys. A similar correlation can be made between composition and mechanical properties as was done previously for the nickel-base alloys. The same holds true for comparison of wrought and cast alloys, as can be expected. Although it is readily apparent that the cobalt-base alloys are lower in strength than the nickel-base superalloys, one must also be cognizant of the fact that, particularly in the cast alloys, the cobalt-base alloys are more stable in the temperature range 1400-1800°F. It is this characteristic of the cobalt-base alloys which makes them more useful at temperatures in excess of 1600°F for longer time applications.

Iron-(Ni-Cr and Cr-Ni)Base Alloys

This class of alloys has suffered most in the superalloy development program. Possibly the lack of interest is due to less glamorous strength properties than those of nickel or cobalt-base alloys, but for applications requiring thermal shock resistance and corrosion resistance to oxidizing and reducing atmospheres they are outstanding.

The chemical composition of these alloys will determine their metallurgical structure and properties. The strongest and toughest alloys are austenitic with various chromium-nickel combinations dictated by service specifications such as high-temperature strength required, resistance to carburization and corrosion, minimum ductility acceptable, tolerances, and cost. The basic strengthening mechanism is carbide precipitation, and the alloys are responsive to heat treatment. Properties such as corrosion resistance, creep strength, and ductility can be controlled by composition (carbon content) and heat treatment to redistribute or alter the shape of the carbides.

Figure 4 shows the effect of temperature on some typical alloys in the iron-nickel-chromium-base group. D-979 contains 45 Ni and can be considered a nickel-base alloy with an appreciable (30 percent) iron content plus molybdenum, tungsten, aluminum, and titanium. The RA-330 and Incoloy T (modification of "Incoloy", Fe-Ni-Cr Alloy) are annealed sheet, and the N-155 (AMS-5376), and iron-nickel-chromium alloy with 20 cobalt, is in the as cast condition. Note that at elevated temperatures the strength of this group of alloys is considerably below that of the two classes of alloys discussed previously.

Stress-Rupture Properties

The discussion of the three alloy systems comprising the superalloys has practically been limited thus far to short time tensile strength at various temperatures and briefly on corrosion resistance. For continuous or intermittent operation for extended periods of time at elevated temperatures, however, creep and stress-rupture properties become the controlling factors.

In the case of nickel-base alloys, the complex compositions permit a wide variance in properties by use of different heat treatments. Optimum heat-treating cycles have been established for a given alloy, dependent upon the specific properties desired. One heat treatment can be specified for maximum short time tensile strength, while another produces optimum creep properties. In the case of the Nimonic alloys, heat treatments have been specified to produce maximum ductility at creep failure. Each heat-treating cycle is dependent upon composition and cannot be used interchangeably between various alloys. There are four basic ingredients in nickel-base superalloys that are affected or interact with the critical heat-treating conditions:

1. Solid solution matrix (gamma)
2. $\text{Ni}_3(\text{Al, Ti})$ gamma prime and Ni_3Ti beta precipitate
3. Carbides (M_6C , M_{23}C_6 , M_7C_3 , TiC)
4. Nitrides (TiCN , CbN)

The basic heat-treating cycle consists of solution treatment followed by aging. From the standpoint of structural stability, the choice of aging temperature is of the utmost importance, and service temperature is the prime consideration.

Figure 5 compares the stress-rupture life of several superalloys in the wrought and cast condition. As has been mentioned previously, although nickel-base alloys are considerably stronger, the cobalt-base alloys such as X40 (HS-31) are more stable at elevated temperatures. This can be expected due to the strengthening mechanism and

the aging phenomena involved; the sluggish reaction of the precipitation of carbides as compared to the precipitation of gamma prime, $\text{Ni}_3(\text{Al}, \text{Ti})$ in the nickel-base alloy systems. Rupture data for the new NASA developed casting nickel-base alloy is not included but is expected to exceed IN-100 slightly. The alloy is not being produced commercially at this time. In the wrought alloys Nimonic 115, one of the latest nickel-base alloys developed by Mond in England, is equal to Udimet 700 in stress-rupture properties.

Thus far, we have discussed briefly the state of the art of superalloys, and merely touched upon applications, problem areas, and anticipated areas of research and development. It is a foredrawn conclusion that the contemplated applications and problem areas will dictate the research and development needs, and map out the course to be taken.

For several years, the continued development of wrought-age-hardenable superalloys has supplied the designer with jet engine materials capable of meeting the requirements at high service temperatures. Recently, however, the designers have become hampered by materials limitations and further improvement is deemed mandatory. Application of these materials has expanded to structural components in airframes and skins and fuel elements, in addition to engine components. Increased acceleration, space environments, and re-entry phenomena have increased the performance requirements of these materials. Materials limitations therefore spearheaded the search for new and improved alloys, but research and development was curtailed somewhat in range due to lack of Government support and limited research funds of private organizations. Nevertheless, great strides have been made, particularly in cast age-hardenable nickel-base superalloys. Alloys inherently stronger in creep-rupture and elevated temperature strength than the corresponding wrought composition have been developed. The pros and cons of wrought versus cast alloys will not be discussed other than to mention that it is generally felt that wrought alloys have increased reliability, shock resistance, and ductility.

One of the major requirements in superalloy development is to develop materials capable of covering the temperature gap between 1800°F and 2000°F. Most superalloys have satisfactory oxidation resistance up to 2000°F and can be coated to increase corrosion resistance to temperatures up to 2300°F. The drastic drop in tensile strength and creep resistance limits their use, however, above 1750-1800°F for wrought alloys and 1800-1900°F for cast alloys. The Air Force is sponsoring a program directed toward developing an alloy or technique capable of producing a wrought material (sheet) with a minimum short time tensile strength of 50,000 psi at 1900°F. For short time applications, strengths in the 45,000-50,000 psi range at 2000°F are considered adequate. A more detailed listing of requirements follows:

AREA I Cheaper and easier to make superalloys for high stress, high temperature applications (2000°F)

- (a) Improved thermal shock resistance of nickel-base alloys.
- (b) Improved strength cobalt and iron-nickel-chrome-base alloys.
- (c) Wrought alloys with strengths and stress-rupture properties equal to cast alloys.
- (d) Casting alloys with a high level of reproducibility which do not require vacuum melting and casting techniques.

AREA II Development of alloys which are strengthened by mechanisms not dependent upon carbide or gamma prime precipitation in order to achieve greater strength-temperature stability.

(a) Investigation of dispersion hardened alloys.

AREA III Investigation of fabrication techniques and processes, and physical and mechanical property evaluation, to establish:

(a) An overall cost reduction in superalloy utilization.

(b) Optimum utilization of maximum mechanical properties by improved joining techniques.

(c) Comprehensive design criteria for the newest and best superalloys available.

Effort expended in Areas I and II should be directed toward reducing the composition complexity and precise controls exercised to achieve minimum specifications for currently available superalloys. The slack in development of cobalt and iron-base alloys should be picked up, and introduction of new alloy systems other than the three basic superalloy systems discussed should be contemplated. In this area, vanadium alloys show promise on a strength-to-weight basis, but impose the problem of catastrophic oxidation at elevated temperatures. Vanadium has the lowest density of the ten highest melting point refractory metals, exhibits good weldability and formability (ductility). The strength-to-weight ratio of V-5Ti-20Cb exceeds that of F-48 (columbium alloy) and Mo-0.5Ti-0.07Zr up to 2200°F and 2000°F, respectively. An attempt to develop chromium alloys for structural purposes is not feasible because of the poor ductility. Ductilizing chromium by a liquid phase sintering process should improve fabricability and joining characteristics, but most of the strength is sacrificed due to the low melting point matrix material. Use of chromium seems destined to remain as an alloy addition or as a coating for oxidation resistance.

In the area of dispersion hardening, there is a basic need to increase the state of technology on dispersion strengthened systems. Along these lines, the Air Force is sponsoring a basic program to investigate the strengthening mechanisms in such systems. An attempt will be made to uncover the basic differences in precipitation-hardening and dispersion-hardening systems, and to investigate the factors influencing the characteristics of dispersion strengthened alloy systems. This information, coupled with the ever increasing technology on dispersion hardening, will enable researchers to conscientiously formulate programs which will eliminate much of the trial and error method adopted since the development of SAP aluminum alloys. Powder metallurgy techniques previously considered somewhat unfruitful, to the point of hopelessness, with respect to the superalloy systems, should be revived. Recent unpublished information indicates the possibility of a nickel-chromium matrix strengthened by thoria to have high strength and stress-rupture properties comparable to some of the best superalloys.

Area III of the proposed requirements is of the utmost importance to the designer. Many of the recently developed alloys have not been fully evaluated from a structural point of view. Several of the commercially available high-strength superalloys cannot be used at their full potential except in the form of precision castings. Development of fabrication and processing techniques will increase their use for structural applications.

The composition complexity of these alloys and the strengthening mechanism involved introduce numerous problems in welding and brazing. Another factor is the limited workability of some of the highest strength wrought alloys such as Udimet 700 which can only be formed into the simplest configurations. Comprehensive investigations such as have been carried out on Rene 41, welding, brazing, and fabrication parameters, are needed.

Specific Air Force requirements emphasize the need for wrought alloys to produce sheet material. The direct aim is to achieve the greatest strength-to-weight ratio possible for the obvious reason of increasing performance characteristics of long range missiles and space vehicles. Weight savings mean longer ranges, faster speeds, and increased economy for every pound of fuel consumed. The use of thin gauge sheet materials will probably require composite structures such as honeycomb to supply the stiffness necessary to prevent buckling at very high stresses. In the temperature range 1400-2000°F, the superalloys have practically no competition as yet, but the possibility of developing titanium alloys in this range exists.

Another area of importance is oxidation resistance. It will be noted that strides have been made in increasing superalloy strength, but composition changes in the most recently developed alloys reveal a marked decrease in chromium content. In some cases, the chromium content has been reduced as much as 50 percent. The result has been a decrease in oxidation resistance. The slight increase in aluminum content reduces the density in some instances, but does not provide a sufficient increase in oxidation resistance to compensate for the decrease due to the reduction of chromium. Although coatings for superalloys may not present an exceedingly difficult challenge, nevertheless, at service temperatures of 1800-2000°F the need does exist. The requirement may be stated specifically, "to increase the oxidation and corrosion resistance at temperatures in excess of 1800°F." Coatings or composition changes may provide the solution.

The versatility of superalloys has contributed greatly to the defense effort. Prime examples are the use of Inconel X in the X-15, as mentioned previously; Rene 41, Waspaloy, Udimet 700, Inconel W, and A-286 in the B-70; and Rene 41 and Inco 702 in the Dyna-Soar re-entry vehicle project. These materials are being utilized in the form of turbine wheels and blades, trusses, tubing and fittings, airframe skin panels, reinforcing structures in elevated temperature areas, to mention a few applications.

Finally, industry cannot be expected to support research and development in these alloy systems completely on its own. This would inevitably provide short range research involving minimum risk and generally producing lesser benefits. Industry cannot afford to venture much capital into such long range plans as are mandatory from the Government's point of view. Such programs should be formulated on a cost-share basis for alloy development and longer range composition, structure, and property studies. One cannot fail to see the benefits which can be derived through such effort, whether viewing the situation through the eyes of the Department of Defense or through the eyes of industry.

BIBLIOGRAPHY

1. "Super Strength Alloys," Metals Handbook, ASM, Vol. 1, 8th Edition, p. 467-511.
2. "Recent Developments in Superalloys," DMIC Memo No. 64, Battelle Memorial Institute, Sep 8, 1960.
3. "Strengthening Mechanisms in Nickel-Base High-Temperature Alloys," DMIC Memo No. 95, Battelle Memorial Institute, April 4, 1961.
4. "Design Information on Nickel-Base Alloys for Aircraft and Missiles," DMIC Rpt No. 132, Battelle Memorial Institute, July 20, 1960.
5. "Evaluation of Nickel-Based Alloys," AEC R&D Rpt UC-25, AGN-TM-361, Aerojet-General Nucleonics, January 1961.
6. Brown, J.T., and Wilson, J.E., "Two New 1800°F Alloys for Cast Turbine Blades," Metals Progress, November 1958, p. 83.
7. Weisenberg, L.A., and Morris, R.J., "How to Fabricate Rene 41," Metals Progress, November 1960, p. 70.
8. Barker, J.F., Coutts, W.H., Jr., and Morris, R.J., "Astroloy - A Superalloy for 1900°F Use," Metals Progress, December 1960, p. 94.
9. Luchok, J., Radavich, J.F., Pennington, W.J., and Maxon, J., "Advances in High-Temperature Materials," Metals Progress, February 1961, p. 91-100.
10. Wilson, J.E., and Radavich, J.F., "Phase Identification in Nickel-Base Alloys," Metals Progress, May 1961, p. 94.
11. "High Temperature Alloy Digest," D-818, Wright Aeronautical Division of Curtiss-Wright Corporation.
12. "Vanadium-Columbium Alloys for Temperatures up to 2200°F," paper, Armour Research Foundation.
13. Greenwald, H., Jr., "Technical Proposal for Nickel Alloy Sheet Development," Vought Aeronautics.
14. Grant, N.J., "Technical Proposal for Investigation of Strengthening Mechanisms in Dispersion Strengthened Materials," Massachusetts Institute of Technology.
15. "Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys," DMIC Memo No. 104, Battelle Memorial Institute, May 5, 1961.
16. "Superalloy Data Sheets", prepared by DMIC, Battelle Memorial Institute for DOD Committee on Metallic Materials for Use Below 1800°F.
17. "The Evaluation of Nickel-Base Precipitation-Hardening Superalloys," DMIC Memo No. 84, Battelle Memorial Institute, February 6, 1961.

TABLE I

NOMINAL COMPOSITION OF VARIOUS NICKEL-BASE SUPERALLOYS

ALLOY	Cr	Co	Al	Ti	C	Fe	Mo	W	B	Zr	OTHER
Nimonic 80	18-21	2.0*	0.5-1.8	1.8-2.7	0.1*	5	—	—	—	—	—
Nimonic 90	18-21	15-21	0.8-2	1.8-3	0.1*	5	—	—	—	—	—
Nimonic 100	10-12	18-22	4-6	1-2	0.3*	2	4.5-5.5	—	—	—	—
Nimonic 105	13-16	18-22	4.2-4.8	0.9-1.5	0.2*	1	4.5-5.5	—	—	—	—
WROUGHT											
Inconel "X"	14-17	1.0*	.04-1	2.2-2.8	.08*	—	5-9	—	—	—	Cb, Cu, S
M-252	18-20	9-11	.75-1.25	2.25-2.75	.1-.2	5*	—	—	.001-.01	—	Cu, S
Waspalloy	18-21	12-15	1.0-1.5	2.6-3.25	0.1*	2*	3.5-5.0	—	.003-.01	.05-.12	—
Rene 41	18-20	11	1.5	3.1	.09	—	10	—	.01*	—	—
Udimet 500	15-20	13-20	2.5-3.25	2.5-3.25	.15*	4*	3-5	—	.01*	—	S
Udimet 700	13-17	17-20	3.75-4.75	3-4	.15*	1*	4.5-5.75	—	0.1*	—	—
Unitemp 1753	15.5-17.5	6.5-8.5	1.75-2.25	2.9-3.4	.2-.28	7-11	1-2	7.5-9.5	.002-.01	.02-.1	S
Astroloy	15	15	4.2	4.0	.10	—	5.8	—	.025	—	—
CAST											
Haynes "713C"	11-14	1.0*	5.5-6.5	0.35-0.9	.08-.2	2.5*	3.5-5.5	—	.005-.02	.05-.2	Cb, S
Inco "717C"	10-11	7-9	7.25-8.0	0.25-1.25	0.2*	2.0*	3.5-5.0	—	.005-.02	.05-.2	Cb, S
Nicrotung	12	10	4.0	4.0	0.10	—	—	8	0.05	.05	—
IN-100	8-11	13-17	5-6	4.5-5.5	0.15-0.20	1.0*	2-4	—	.008-.02	.03-.09	.7-1.2V
NASA TN-D-260	6	—	6	—	0.15	—	4	4	—	1	2.5V, 8Td

* Maximum

Nimonic series are English wrought alloys.

TABLE 2
NOMINAL COMPOSITION OF VARIOUS COBALT - BASE SUPERALLOYS

ALLOY	Cr	Ni	C	Mo	W	Ta	Ti	B	Co	OTHER
WROUGHT										
J-1570	20	28	0.20	—	6	—	4	—	Bal.	—
J-1650	19	27	0.20	—	12	2	3.8	.02	Bal.	—
CAST										
HS-25(L-605)	20	10	0.15	—	15	—	—	—	—	2Fe, 1.5Mn, .5Si
Stellite 31	25.5	10.5	0.50	—	7.5	—	—	—	—	2Fe*, 1Mn*, 1Si*
Haynes Alloy No. 151	20	—	0.55	—	12.5	—	—	—	Bal.	—
W1-52	21	1	0.45	—	11	** 4	—	—	Bal.	2Fe, .5Si*, .5Mn*
S816	20	20	0.40	4	4	—	—	—	—	4Fe, 4Cb, 1.2Mn, .4Si
Mod. S816 + B	20	5	0.4	4	4	** 4	—	1	Bal.	2Fe*, .4Si, 1Mn

* Maximum

** Ta + Cb

Balance of all alloys is nickel.

STRENGTH TO WEIGHT RATIOS OF VARIOUS ALLOYS

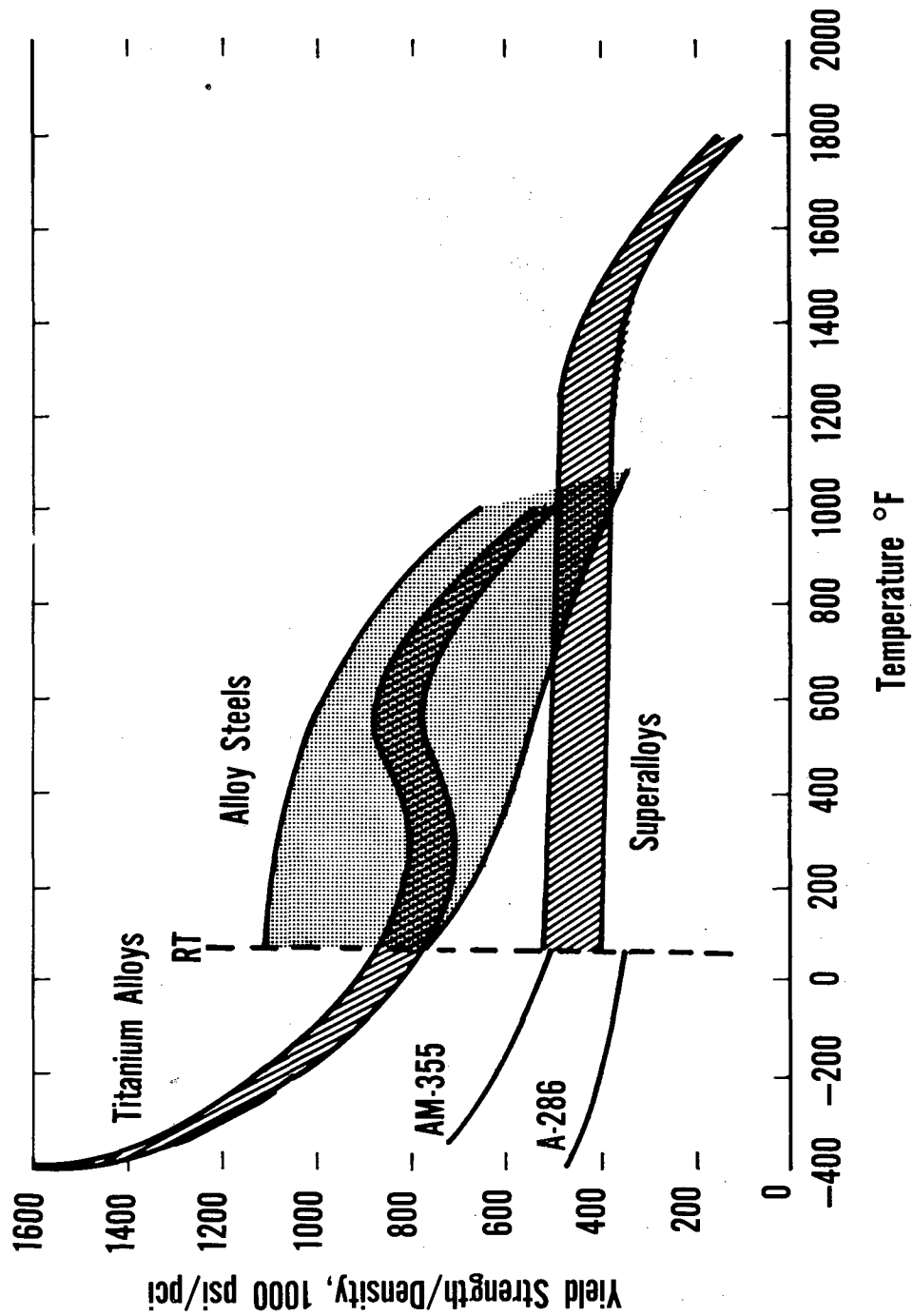


Figure 1. Strength to Weight Ratios of Various Alloys

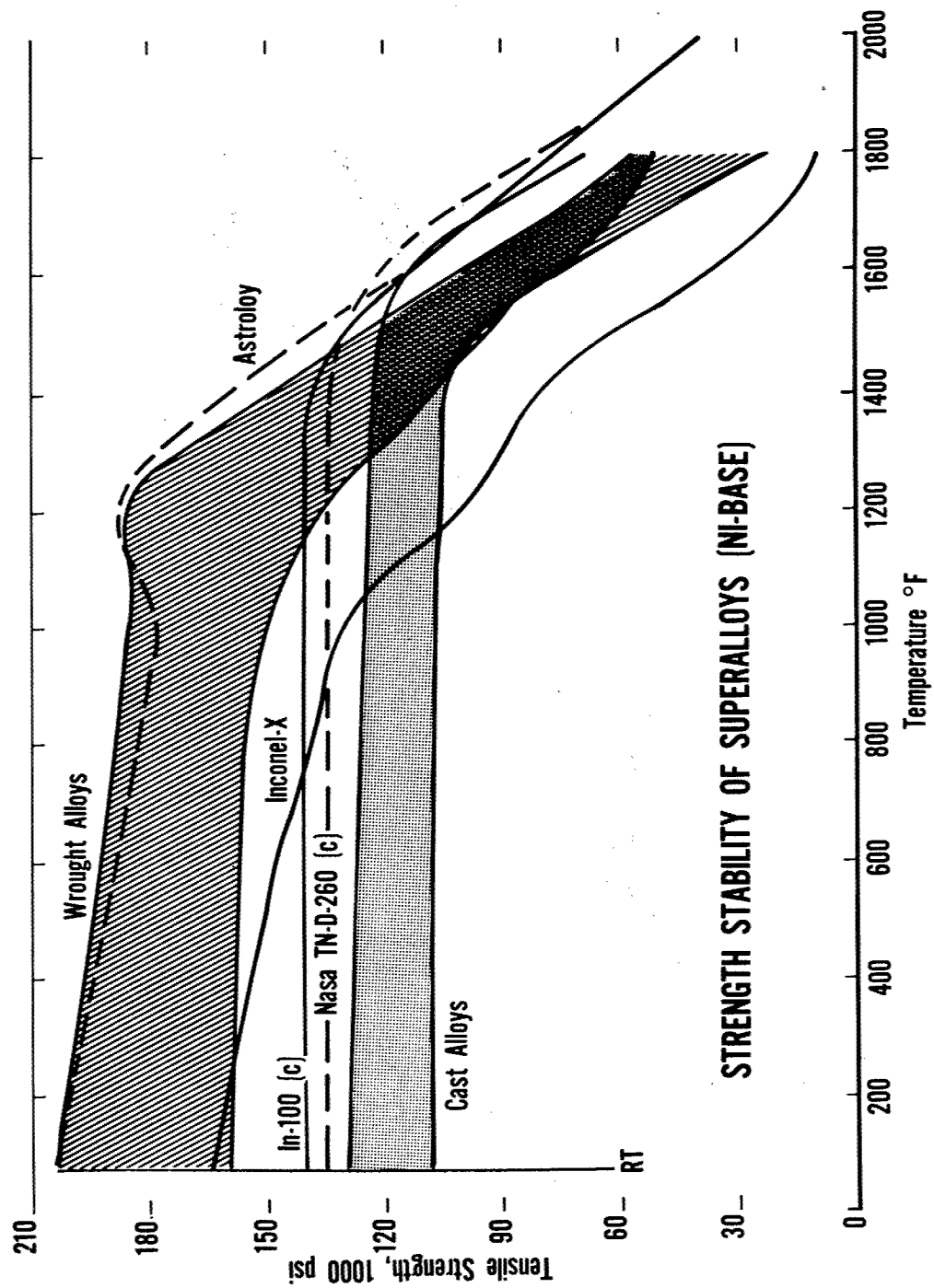


Figure 2. Strength Stability of Superalloys (Ni-Base)

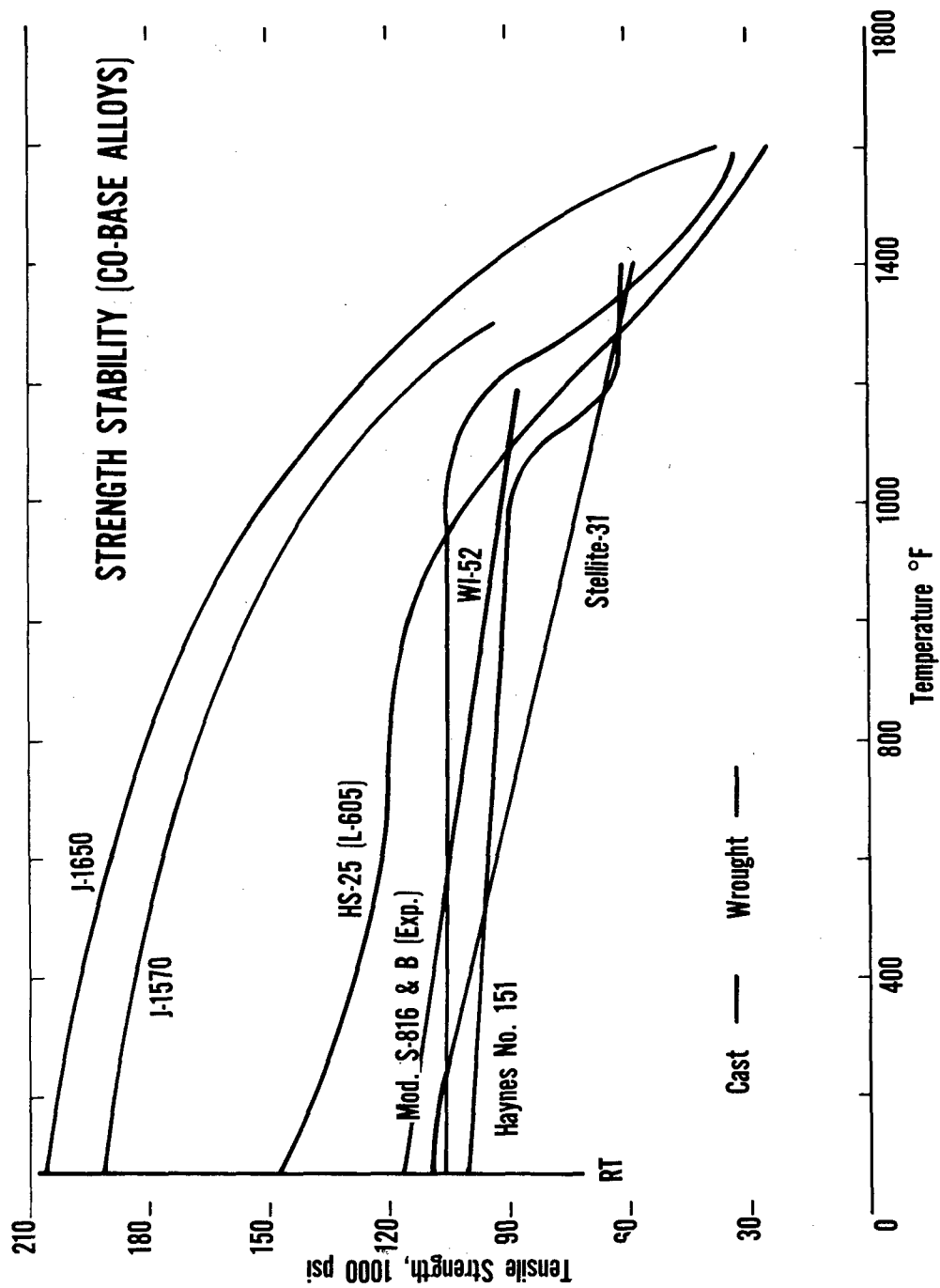


Figure 3. Strength Stability (Co-Base Alloys)

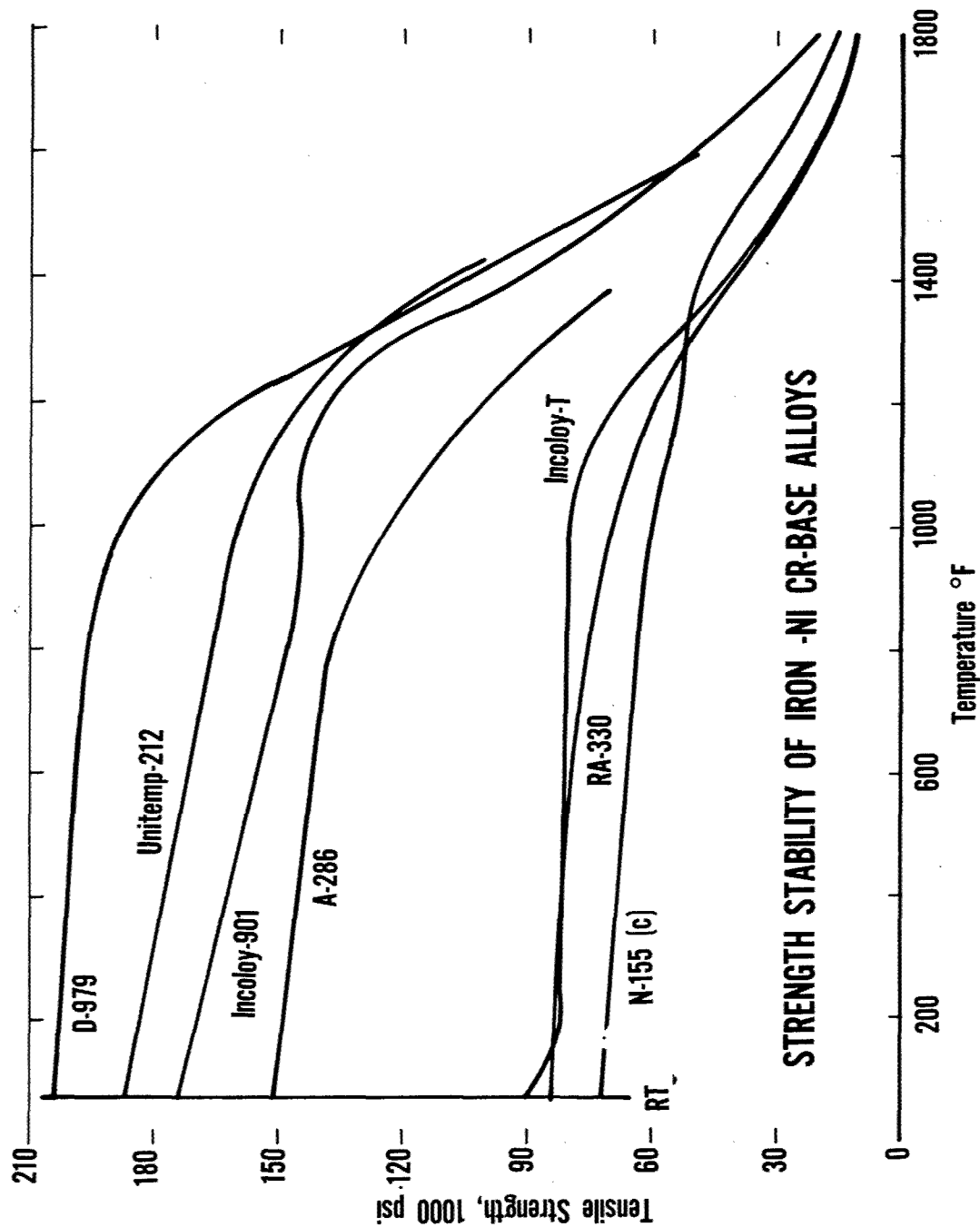


Figure 4. Strength Stability of Iron-Ni-Cr-Base Alloys

SUPERALLOY STRESS RUPTURE STRENGTH

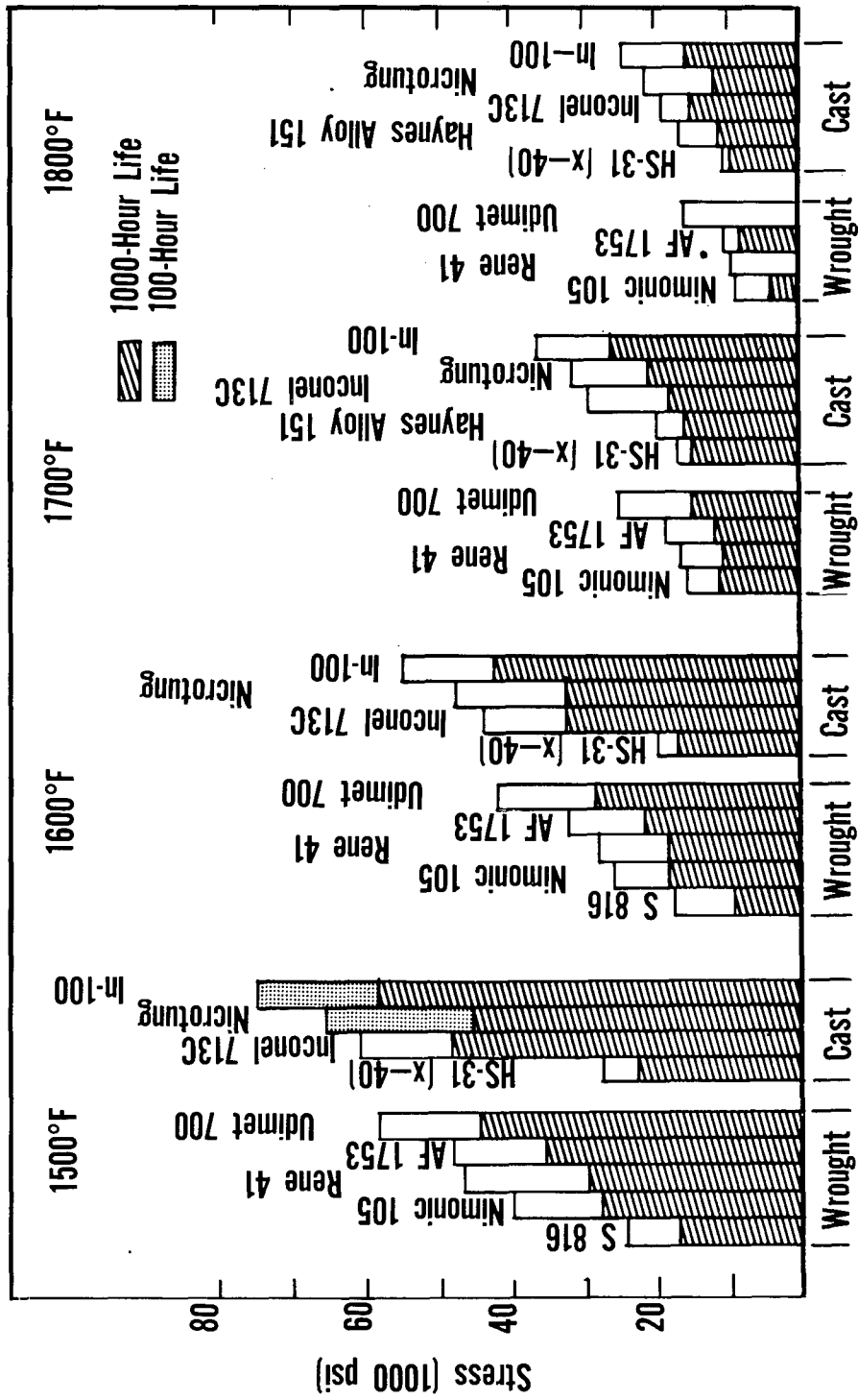


Figure 5. Superalloy Stress Rupture Strength

STRUCTURAL MATERIALS TO 1800°F (STEEL AND TITANIUM)

P.L. Hendricks

Directorate of Materials and Processes, ASD

In choosing materials for applications in present and future weapon systems, design requirements are of prime importance. Without attempting to assess the relative importance of each, they are listed as follows: high strength-weight ratio, ductility and fracture toughness, stability, fabricability, and corrosion resistance. There are certainly many other factors of importance; however, many of these will be determined by the intended application and the type of environment envisaged. Since it is impractical to attempt to cover the entire spectrum of available materials, this discussion will be limited to steel and titanium alloys for applications at temperatures up to 1200°F.

Three broad categories of steel will be discussed: low alloy martensitic steels, hot work die steels (primarily H-11 types), and the stainless steels. One other class of materials to be considered are the iron base alloys containing 20 to 25 percent nickel. These alloys may or may not be classified as steels, depending almost entirely upon a matter of definition. Typical strengths currently available in steels from room temperature up to approximately 1200°F are shown in figure 1.

We turn our attention first to a discussion of steel and consider the low alloy martensitic steels, typified by such compositions as 4340, AMS 6434, and D6A. These steels exhibit tensile strengths in the 300,000 psi range with good ductility as measured in the uniaxial tensile test. These materials depend to a great extent for their strength upon the amount of carbon present. A wide variety of properties may be obtained, depending upon a judicious selection of heat treatment. Since materials with high strength-to-weight ratios are of considerable interest, it should be observed that most of these materials are tempered in the lower range (400-600°F) in order to achieve high strengths. It is therefore apparent that the application of these materials must be limited primarily to room temperature applications or very moderate elevated temperatures. It should also be observed that the carbon content in these steels, as well as others, plays a dual role: (1) contributing to high strengths; and (2) contributing to a decrease in ductility and toughness. The role of carbon is mentioned because of its significance and will be further related to material properties in the discussion. In summarizing, the low alloy martensitic steels provide very high strengths and are useful for room temperature and very moderate elevated temperature applications.

The H-11 steels form part of a class known as the hot work die steels. While there are several classes of hot work die steels, only the H-11 types will be discussed. The chemical composition range of this group of steels is C - .30-.40, Mn - .20-.40, Si - .80-1.20, Cr - 4.75-5.50, Mo - 1.25-1.75, and V - .30-.50. These steels are characterized by: (1) high strength to density ratios in the 1000°F range; (2) sufficient hardenability to permit air quenching; and (3) tempering temperatures in the 1000 to 1100°F range. These characteristics, and others, make them usable for many applications in aircraft and missiles. Some limitations of these steels are: (1) possible low transverse ductility; (2) sensitivity of mechanical properties to carburization or decarburization. The H-11 steels can be heat treated to strengths from 280,000 to 300,000 psi tensile, with reasonable ductility as measured in the uniaxial tensile test. Much attention is being given to this class of material as a candidate for many current and future weapon systems.

The stainless steels comprise a large group of materials from which a variety of properties may be obtained. Since some classes are of more interest than others in present applications, only a few will be mentioned here very briefly. The semi-austenitic precipitation-hardenable stainless steels offer yield strengths in the neighborhood of 200,000 psi and retain a usable proportion of their room temperature strength up to about 900°F. The limiting temperature depends upon the alloy, the application, and duration of exposure at elevated temperature. The austenitic precipitation-hardenable stainless steels have been used mainly in applications requiring exposure to temperatures of 900 to 1200°F. These materials retain a large proportion of their room temperature strength at temperatures in this range. Other types of stainless steels are the martensitic and austenitic types. The austenitic types are further subdivided into austenitic precipitation-hardenable steels and austenitic stainless steels deriving their strength through cold working of the alloy. The stainless steels as a group are a very important part of the materials spectrum and offer properties for applications from sub-zero temperatures up to temperatures slightly in excess of 1200°F.

In the discussion of steels to this point, it is fairly evident that a large number of compositions is available offering a range of properties over temperatures from cryogenic conditions to slightly above 1200°F. While emphasis previously was placed on strength and ductility, other properties such as creep-rupture, stability, fatigue, and corrosion resistance should be adequately provided for by making a judicious choice of materials for a particular application.

Since considerable emphasis has been placed on strength-weight ratios, what are the requirements in this area? The designers are presently asking for materials with yield strength to density ratios of 1,000,000 or higher. Yield strength to density ratios of some currently available steel and titanium alloys are shown in figure 2.

In checking the available conventional steels, it is apparent when considering usable properties, there are no steels presently that meet these requirements. What then are the possibilities of meeting these requirements?

With our present knowledge, materials with yield strengths to meet these requirements may be possible if we make use of exotic fabrication practices such as "ausworking", about which we have a limited knowledge. "Ausworking" is a process of deforming a steel within the lower austenitic bay of the TTT diagram followed by quenching and tempering. This process is applicable to certain low alloy martensitic steels and currently has accounted for tensile strengths in excess of 400,000 psi with yield strengths of at least 350,000 psi. There are certain other questions related to the properties of such materials, but these are also related to conventionally treated compositions and will be discussed more fully later in this discussion.

An ausworked steel such as H-11 with a yield strength of 360,000 psi would provide a yield strength/density ratio of approximately 1,300,000. This is approaching the properties for resin bonded glass fibers, used for pressure vessels, but it is postulating a nonexistent production technique. There appear to be other approaches that may produce similar results, one of which is the interaction of a shock wave with a metal. One case reported using the technique where tensile strengths of 600,000 psi in steel has been reported. No information relative to other properties was reported.

Another process known as "mar-straining" is being investigated, which should also produce increases in strength. This process consists of straining of tempered martensite followed by another temper. These illustrations are used to indicate that for yield

strength/density ratio, there are several current thermal-mechanical processes available whose further development may form the basis for obtaining yield strength to density ratios well over 1,000,000 in various steel compositions. Figure 3 shows projected yield strength to density ratios that may be possible in the very near future with the accomplishment of additional research.

Earlier in the discussion, the dual role of carbon content as related to mechanical properties of high strength steel was mentioned. In many of the current steels of interest, a major portion of the strength is derived from the carbon content. Since carbon has a deleterious effect upon ductility, the production of higher strengths by increasing the carbon content would not be the best approach since very low ductility accompanies any major increases in strength. Figure 4 shows the general effect of increasing carbon content on strength and ductility. With this information in mind, a new approach should be made to the development of steels which obtain strengthening by mechanisms, other than those based upon the presence of carbon in moderate amounts. Compositions presently under development indicate this achievement is not entirely futile.

The series of alloys under development are iron base alloys with low carbon and nickel content ranging from about 18 to 27 percent. Response to precipitation hardening is obtained from controlled additions of titanium and aluminum. These materials are hardened by solution treating at about 1500°F and aging at 800-950°F. A refrigeration treatment prior to the aging may be necessary to insure complete transformation. Yield strengths of over 260,000 psi with 6 percent minimum elongation are obtainable with present compositions. In addition, they give promise of excellent toughness with a notch strength ratio in excess of 1:1 even at yield strengths approaching 300,000 psi. Perhaps the good toughness characteristics can be associated with the low carbon martensite formed. The principle of low carbon martensites with additional strengthening by some other mechanism could be logically extended to the development of additional high strength steel compositions.

In the discussion of high strength steels, it was mentioned that certain other material properties would be discussed. Since these properties are also related to titanium alloys, it is proposed that they be further deferred until after a brief look at titanium alloys for application in present and future weapon systems.

Titanium is a light weight, corrosion-resistant, structural material which can be strengthened through alloying. Titanium alloys fall into three categories: (1) alpha; (2) alpha-beta; and (3) beta. Figure 5 shows typical strengths of these classes of alloys. Alpha alloys, such as Ti-5Al-2.5Sn, have medium strength at room temperature and maintain high strengths at temperatures from 800 to 1000°F. They are readily welded and are not heat treatable but maintain toughness to cryogenic temperatures. A wide range of properties is available in the alpha-beta alloys. Alpha-beta alloys can be heat treated to high strength levels; however, welding is considered a problem except in alloys containing small amounts of beta stabilizers, such as Ti-6Al-4V. The heat treatable beta titanium alloy Ti-13V-11Cr-3Al is very ductile and formable and is capable of being heat treated to high strength levels. It becomes brittle at cryogenic temperatures but can be used for short time applications at temperatures up to 1000°F. For longer time elevated temperature applications, the temperature should not exceed 600°F. There are a number of titanium alloy compositions available; however, it is necessary for purposes of this discussion to limit the number under consideration.

By reason of extensive experience with 6Al-4V in aircraft and aircraft engines, one could call it the 4340 of titanium alloys available today. It can be readily forged, and in

the solution treated, quenched and aged condition, the alloy develops tensile minima of 155,000 psi yield strength, 170,000 psi tensile strength, and 5 percent elongation. There are certain indications that Ti-6Al-4V can be processed by cold rolling and aging to a yield strength of 160,000 psi. At a density of 0.161 lb per cu in., this gives a yield strength to density ratio of 1,000,000. In some forming methods, such as flow turning, considerable difficulty is anticipated with the Ti-6Al-4V and alpha-beta alloys in general due to their greater resistance to deformation as compared to the all beta alloys.

The beta titanium alloy B120VCA (Ti-13V-11Cr-3Al), is an extremely attractive material based on present property data. In the annealed condition, it is a medium strength (120,000 psi yield strength) very formable alloy. It can be hardened by an aging treatment to have yield strengths in excess of 180,000 psi. With a density of 0.174 lb/cu in., the alloy exhibits a yield strength to density ratio in excess of 1,000,000 psi/cu in. This is the only material discussed so far that in its present state of development has reached the magic number of 1,000,000. There is also reason to believe that the beta titanium alloy is capable of significantly higher yield strengths than the present 180,000 psi level. The achievement of this strength level would provide yield strength to density ratios somewhat in excess of 1,000,000. The beta alloy is one of the more promising titanium alloys; however, present experience indicates the need for much additional information about the alloy in order to utilize it.

Another titanium alloy worthy of mention is Ti-22.5Cb-12.5Al-5Hf, which is still in the experimental stage. The importance of this alloy does not stem from high yield strength to density ratios or application in the temperature ranges under discussion in this paper, but in the fact that the alloy shows the potential of greatly increasing the temperature range over that normally thought to be useful. Recent work with this alloy has indicated that it may have applications at temperatures up to 1800°F. This is really sensational for a titanium alloy, since they were believed to have reached their limit at considerably lower temperatures. The short time properties of this alloy at 1800°F are: 59,300 psi tensile strength, 49,000 psi yield strength, and 35 percent elongation. Figure 6 compares this alloy on a strength to density basis with other elevated temperature alloys. It should be emphasized that this alloy is still very much in the experimental stage and no predictions as to future use can be made. It is merely mentioned as a matter of interest.

Now that a cursory look has been taken at available steel and titanium alloys, consider briefly another characteristic of these high strength materials imposing a serious limitation, relative to their successful application in present and future weapon systems. This is the problem of fracture toughness, which has been referred to earlier in the discussion. It has been shown that insofar as strength, ductility, strength/weight ratio, etc. are concerned, there are many attractive alloy systems. When attempts are made to utilize these alloys in ranges approaching their maximum yield strengths, they fail to meet requirements primarily because of inadequate toughness. This failing is common to steel and titanium alloys alike and is of particular importance when applied to the production of thin walled pressure vessels. Fracture toughness is essentially concerned with the tolerance of materials to sharp flaws or cracks. Materials with inadequate toughness fail in many instances at stress levels far below the design strength in a brittle manner (100% cleavage failure). A realization of the importance of this parameter has led to considerable study in an attempt to understand better the phenomenon and find means of overcoming or alleviating its drastic effects. In order to speak briefly about the fracture toughness problem and methods of obtaining quantitative data, it is necessary to oversimplify the subject greatly.

In getting an index of the toughness of a material, values known as G_c and K_c are used where:

$$K_c^2 = EG_c = \pi \sigma^2 a$$

$$G_c = \frac{\sigma^2 W}{E} \tan\left(\frac{\pi a}{W}\right)$$

For a more precise determination of G_c , the plastic zone correction should be used, giving rise to:

$$G_c = \frac{\sigma^2 W}{E} \tan\frac{\pi a}{W} + \frac{EG_c}{2W \sigma_y^2}$$

$a = \frac{1}{2}$ crack length

W = width of the specimen

σ = greatest principle stress

E = Young's modulus

K = stress intensity factor at point of instability

G_c = critical driving force per unit area fractured at the point of instability

Minimum G_c or K_c values, thought to be necessary for satisfactory performance in a pressure vessel were agreed upon after much experimental work. Work accomplished by various research groups indicate when K_c values of at least 150,000 psi/inch and yield strengths up to 220,000 psi are used to fabricate pressure vessels, satisfactory performance can be expected (G_c 750 in. lbs/in²). These figures are not absolute but tend to reflect to a degree the thinking of others who have accomplished work in this area.

In looking over the available high strength alloys (steel and titanium), it appears that G_c values show a decrease as the strength of the material increases. This represents quite a problem since to obtain yield strength/density ratios in excess of 1,000,000, it is necessary to utilize these materials at very high percentages of their yield strength. Figure 7 shows G_c values and yield strengths of a current material.

The role of carbon in high strength steels has already been mentioned. In an attempt to relate the carbon content of steels to fracture toughness, it is significant that high carbon contents have a detrimental effect on the fracture toughness. The advantages of low carbon martensites with some other type of strengthening mechanism are again apparent.

The difficulties related to fracture toughness and high strength metallic materials are of prime importance and the problem is receiving considerable attention. The Metals and Ceramics Laboratory is currently sponsoring work to make a detailed study of the initiation and propagation of cracks in high strength steels and titanium alloys. This program is being approached from a metallurgical viewpoint rather than that of pure fracture mechanics. Considerable emphasis is being placed upon fundamental studies of microstructure as related to crack initiation and propagation.

It should be noted that in addition to improving the fracture toughness of high strength materials, it is also necessary to improve fabrication and inspection techniques. Failures encountered in pressure vessels have originated at some flaw which is usually the result

of fabrication processes. Methods of detecting these flaws and means of reducing them to a minimum in both size and quantity is mandatory.

Assuming that it is possible to produce high strength steels and titanium alloys with adequate strength/density ratios and fracture toughness, there are other areas that will require more work.

High strength space age materials are difficult to fabricate. This is especially true of high strength steels. Cutting any steel at Rockwell C-50 or higher is difficult even for external surfaces and is even more difficult for internal boring, tapping, and end milling. Although there is little likelihood that machining in the heat treated condition can be eliminated, designers should consider the advantages of machining closer to the finish size while the material is still in the annealed condition. While conventional machining methods will not be abandoned completely, it is necessary to implement existing techniques with new approaches. Some of these may include sub-zero machining, flooding the part with CO₂ mist, grinding, chemical milling, spark arc processes, and electrolytic machining. The high strength metals present a challenge in the machining and fabrication area; however, it appears that they are not insurmountable and will be solved through perseverance and ingenuity.

With the use of high strength metals at high percentages of their yield strength, joining is a problem that must be faced. Certainly, in some materials conventional welding appears to be impossible since a loss of strength is imminent when the material is heated to the welding temperature. In some instances, it may be possible to alleviate the joining problem through careful design of the components. New brazing alloys and techniques may be useful in many applications. New unique approaches to joining, such as ultrasonics and explosive welding, may find certain applications. Certainly, more basic information relative to the welding process from the metallurgical viewpoint, such as directional solidification effects, effects of contaminants, gas metal reactions, and other factors, would provide long range benefits in the utilization of high strength steel and titanium alloys. There still remains the requirement for the optimization of welding parameters in particular cases where the process is applicable.

These constitute only a few of the areas where additional information concerning the properties and behavior of high strength steel and titanium is required for application in future weapon systems. Additional information is necessary in other areas such as the mechanical properties and behavior for long time applications up to perhaps 30,000 hours, stress corrosion characteristics of many of the steel and titanium alloys, the effects of surface conditions and coatings, to name just a few. All of these factors will certainly play important roles if the potential of high strength steel and titanium alloys is to be realized. The broad categories requiring additional research and information are listed in figure 8.

Great strides have been made in the production of high strength metals for applications up to 1200°F; however, an understanding of the various other factors necessary in their application has not kept pace. The importance of these factors is now realized and work is being done in these vital areas. A start in this direction has been made and future developments in these and related areas should contribute to a brighter outlook for the production and application of high strength steel and titanium alloys in future weapon systems.

REFERENCES

1. Transactions of the ASME, "Minimum Toughness Requirements for High Strength Sheet Steel," March 1961.
2. Metal Progress, "For Stronger Missile Cases -- Decarburize!", March 1961.
3. ASTM Bulletin, "Fracture Testing of High Strength Sheet Materials", January 1960.
4. DMIC Report 116R, September 1960.
5. DMIC Report 137, September 1960.
6. Crucible Titanium Manual, Crucible Steel Company of America.
7. Journal of Metals, "Materials for Space Pressure Vessels", March 1961.
8. Symposium, "High Strength Steels for the Missile Industry", Golden Gate Metals Conference, February 1960.
9. Navord Report 6496, "Progress Report on Fracture Toughness of High Strength Sheet Metals", May 1959.
10. DMIC Report 112, May 1959.

TENSILE STRENGTH VS. TEMPERATURE OF CURRENT STEELS

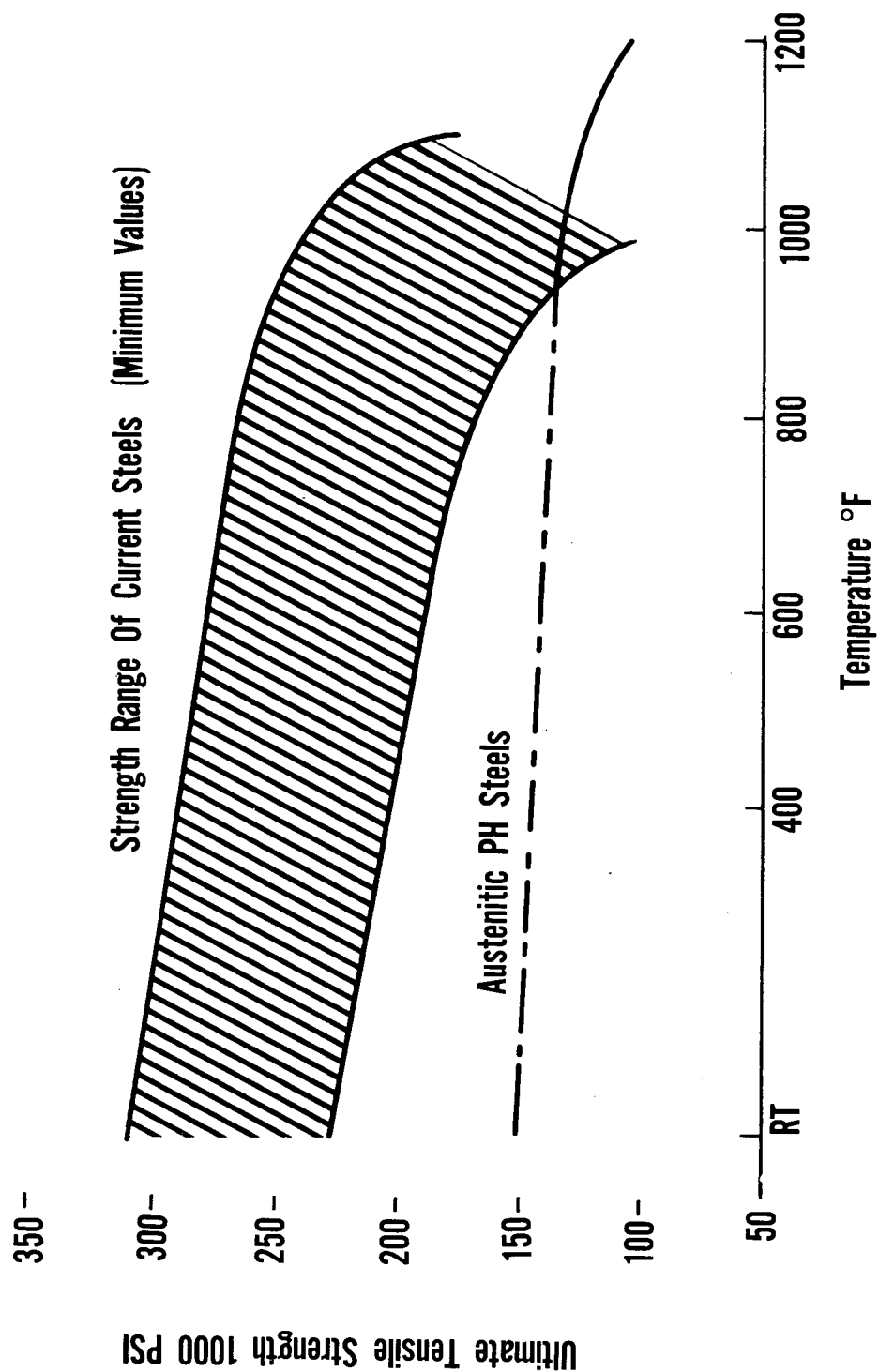


Figure 1.

STRENGTH-WEIGHT COMPARISON OF CURRENTLY AVAILABLE MISSILE CASE MATERIALS

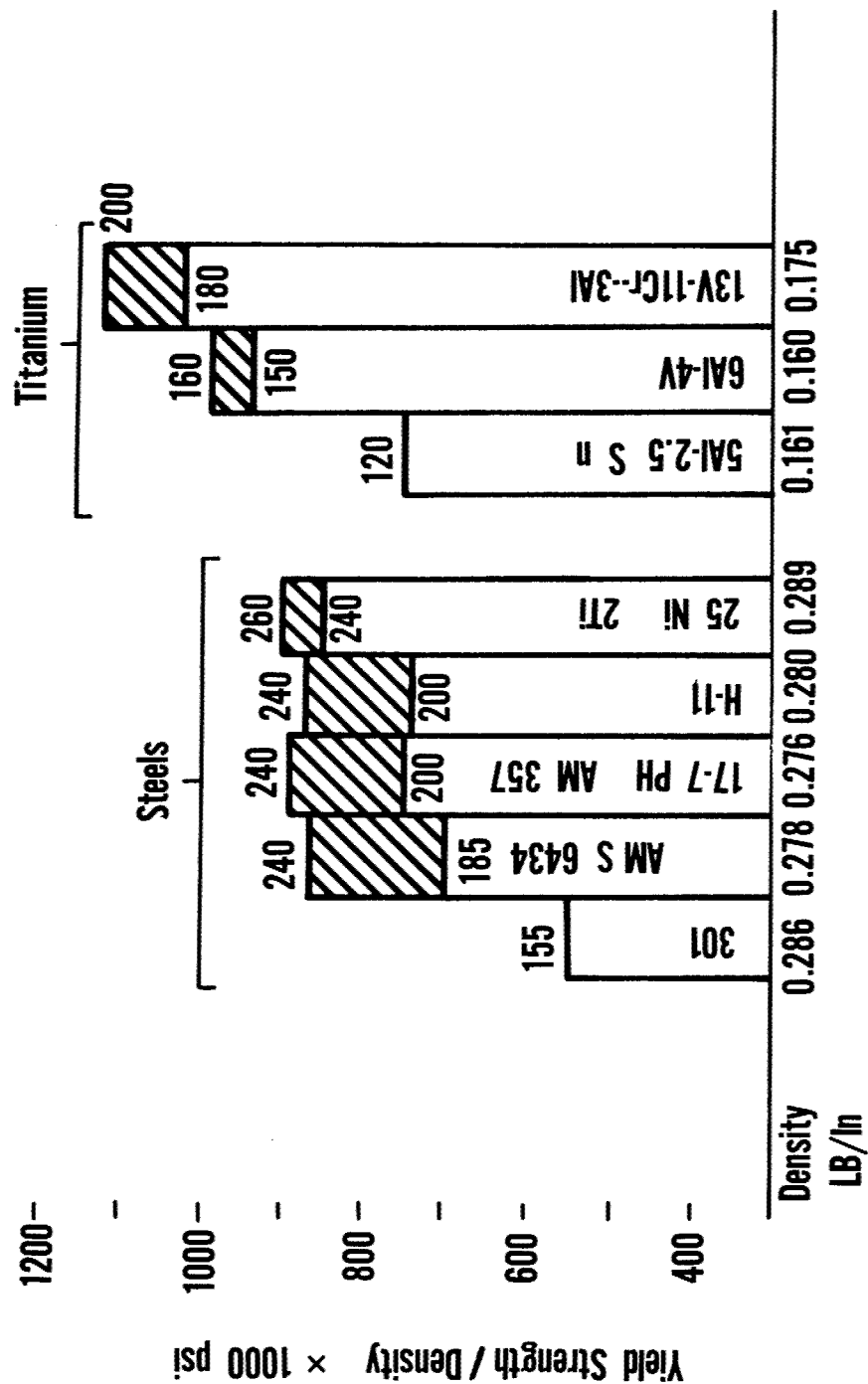


Figure 2.

PROJECTED STRENGTH-WEIGHT COMPARISON OF CURRENT MISSILE CASE MATERIALS

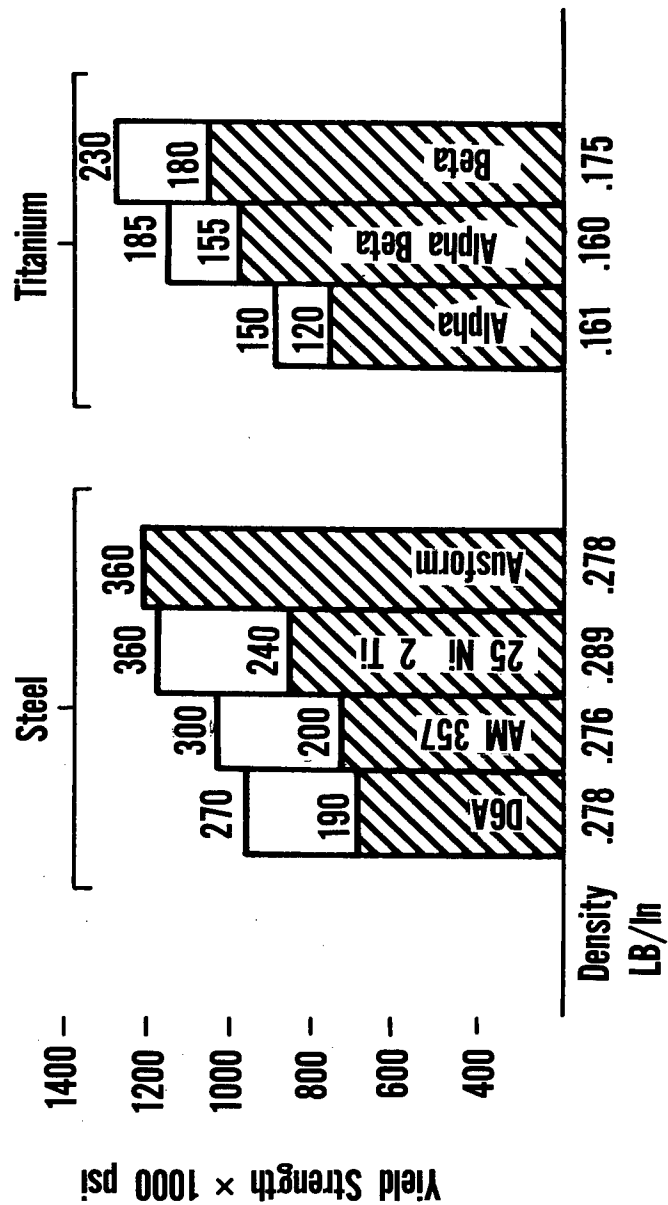


Figure 3.

EFFECT OF CARBON CONTENT ON STRENGTH & DUCTILITY OF STEEL

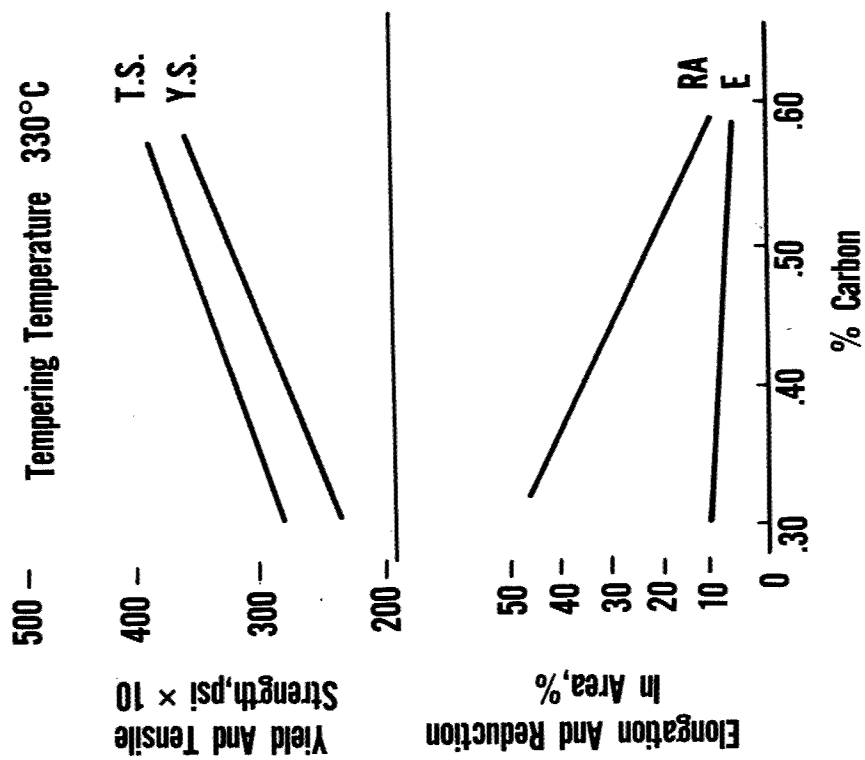


Figure 4.

TYPICAL STRENGTHS OF TITANIUM ALLOYS

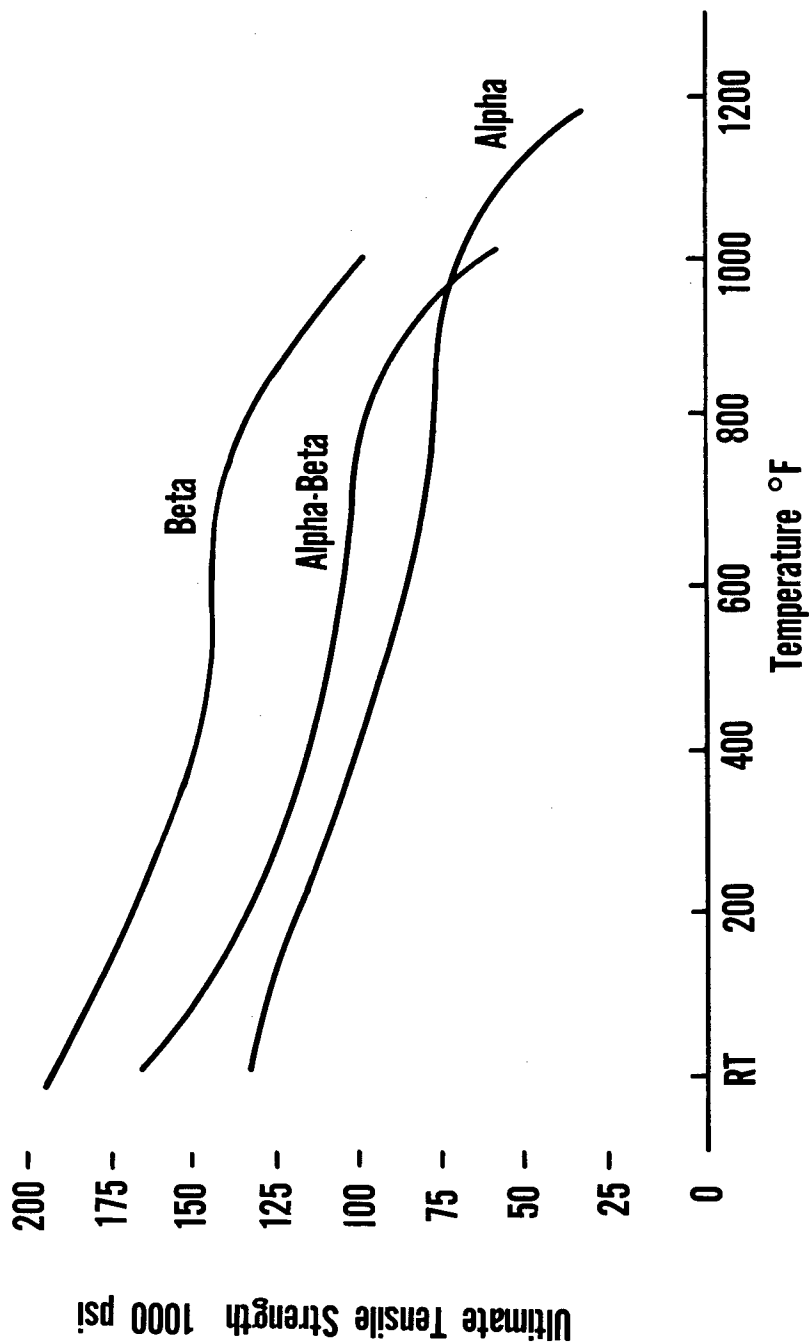


Figure 5.

TENSILE STRENGTH DENSITY RATIO OF ELEVATED TEMPERATURE ALLOYS

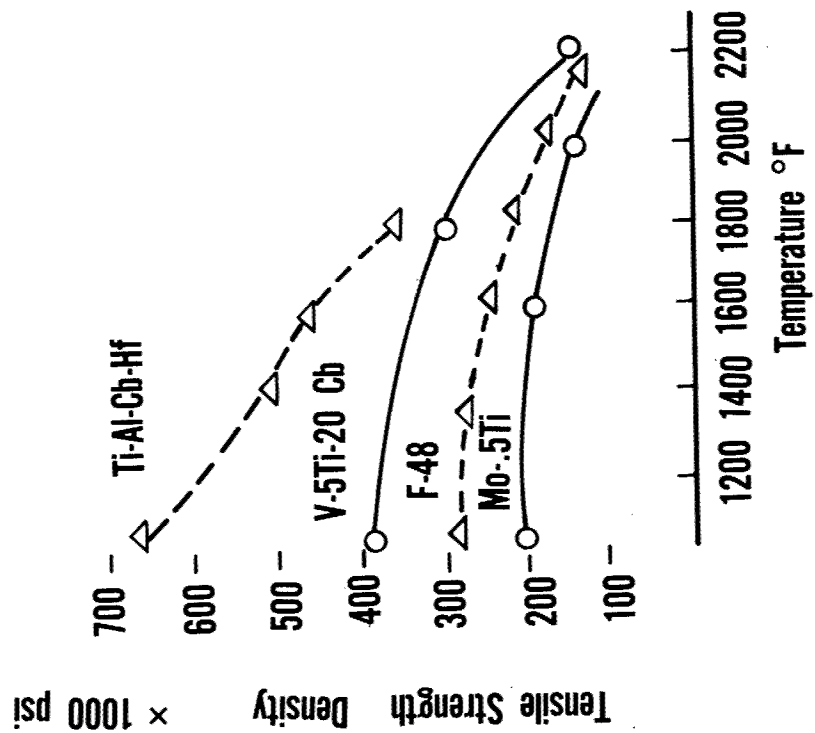


Figure 6.

YIELD STRENGTH & TOUGHNESS OF LADISH D 6A STEEL

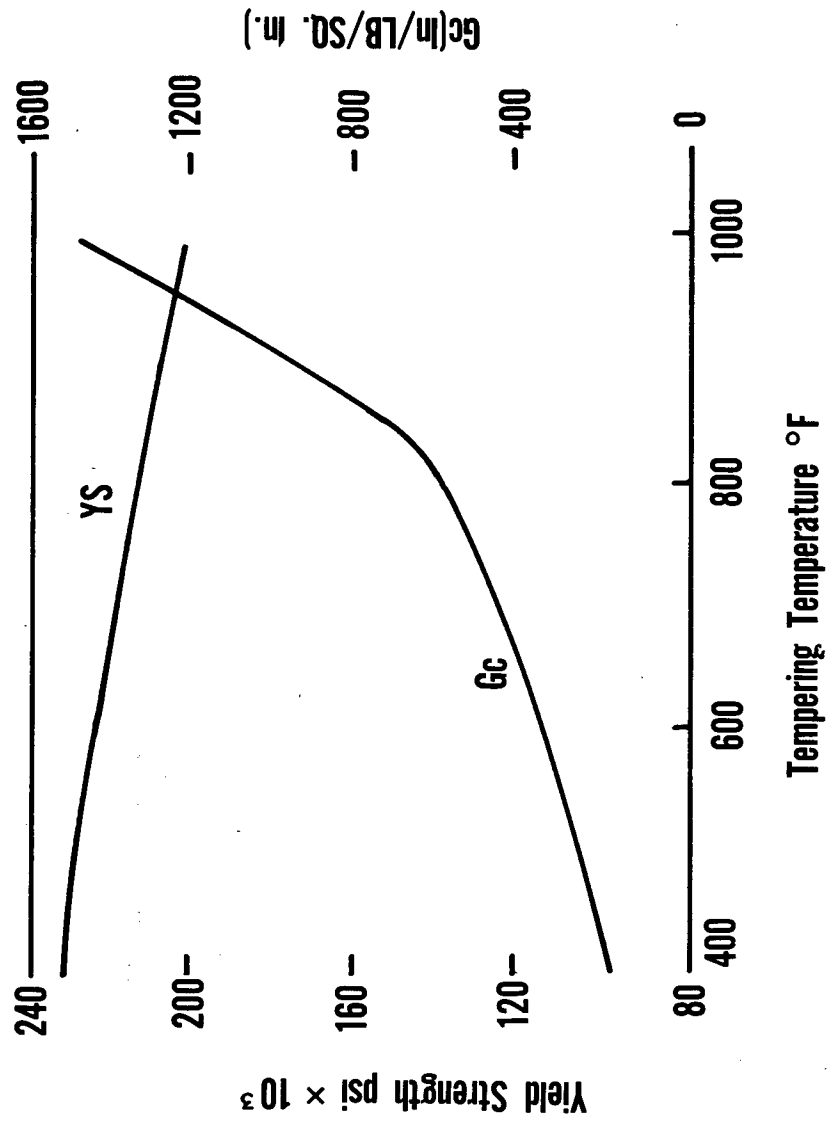


Figure 7.

AREAS REQUIRING ADDITIONAL INFORMATION STEEL & TITANIUM

- **Strength And Ductility**
- **Alloy Development**
- **Joining**
- **Environmental Data**
- **Stress Corrosion Characteristics**
- **Surface Effects**
- **Improved Inspection Techniques**
- **New Maching Techniques**
- **Forming And Fabrication Studies**

Figure 8.

GRAPHITE

Chairman

Mr. W.G. Ramke

Speaker

Capt. R.H. Wilson

Panel Members

Capt. J. Giancola

Mr. J.J. Krochmal

GRAPHITE

Captain Ray H. Wilson

Directorate of Materials and Processes, ASD

The importance of graphite is rapidly increasing as thermal environments become severe and the capabilities of other materials are exceeded. Graphite has interesting potential in this area as it is one of the few materials available with useful strength above 3000°F. When its light weight is considered, graphite becomes even more interesting as an aerospace material; on a strength-to-weight-ratio basis it stands alone above 3100°F. Although graphite has had a primary role in many industrial high temperature structural applications, several challenges to its extensive use and development for aerospace applications have been its unreliability (reproducibility and uniformity), low oxidation resistance, and "brittle fracture." These factors along with a general lack of understanding of the material, how to design for its strong features and around its undesirable features, and the necessity of using off-the-shelf grades of graphite have handicapped its use. This material should not be considered a shelf item in the more demanding aerospace applications. In the past this has been a necessity because this low volume market presented insufficient incentive for the graphite industry to tailor materials for these applications. This does not apply to pyrolytic graphite for the nature of the vapor deposition process makes it a custom made material. It is now apparent that the widely varying properties of polycrystalline graphites can be controlled, and that such properties can be tailored to meet specific materials applications.

For this reason graphite should be discussed in terms of specific or representative aerospace uses. In addition to so-called conventional bulk graphites, many new types of graphites have been developed in useful sizes during recent years and newer graphites are being developed at a rapid pace. The purpose of this paper is to review the state of the art as it applies to Air Force materials applications and attempt to establish the trends and potential of this material in meeting aerospace requirements.

Graphite and its Fabrication

To avoid any misunderstanding the word "graphite" should be explained. Strictly applied, "graphite" describes a particular form of crystalline carbon structure; but common usage more often refers to carbon materials that are characterized by a high content of graphitic carbon. This graphitic form of carbon is illustrated in figure 1. The carbon atoms are arranged in benzene rings bonded by strong covalent forces and in this direction (a-direction) the crystal is very strong. The layers formed by these rings are bound by much weaker van der Waal's forces and the crystal is very weak in the direction perpendicular to the layer planes. This anisotropy also has a similar affect on other properties. For example, thermal and electrical conductivity are high parallel to the benzene planes (a-direction) and low perpendicular to the planes (c-direction). Thermal expansion is low in the parallel direction and high in the perpendicular direction. Manufactured graphites are made up of crystallites of the structure described, but the preferred orientation of the crystallites within a piece may vary from near random orientation to a high degree of preferred orientation.

In a typical manufacturing process graphite is made by mixing calcined petroleum coke (the filler material) and coal tar pitch (the binder material). Shapes of this mixture are formed by extrusion or molding and the pieces are heat treated to 1400-1700°F in the baking cycle and then to 4500-5400°F in the graphitization cycle. This short description omits many of the process variables used to achieve the variety of properties available in the various bulk grades. In the carbon industry these process variables or tricks of the trade are closely guarded secrets. Nevertheless the process as generally described above is typical in the industry.

Raw Materials: Almost any organic material that leaves a high carbon residue when heated can be used to make graphite; however, petroleum cokes are the primary filler raw materials used in the industry. The selection of a particular coke might depend upon a number of considerations; however, in general the major reasons for their use are low cost, relatively low impurity content and ease of graphitization. These factors outweigh the disadvantages associated with a nonreproducible by-product raw material so far as the vast majority of the industrial market is concerned. Some of the things that effect the physical and chemical properties of the coke and also the final graphite piece are the source of the crude oil, refining operation, and coking conditions. It would be desirable to have more control over this raw material but this type of cooperation is seldom compatible with the objectives of the petroleum industry. Synthetic cokes prepared from aromatic hydrocarbons would overcome these problems but economic considerations are a big deterrent to their use. Particle size, shape and distribution also influence subsequent processing and the final product. Lampblack and various types of coke may be used when specific properties are desired. The cokes are calcined to remove volatile hydrocarbons and shrink the fillers material before incorporating them into a formed piece. The common binder material is coal tar pitch. Again this by-product material is conveniently cheap and leaves a high carbon residue. It is thermoplastic, solid at room temperature, and softens at approximately 200°F. This property permits the mixing and forming of shapes in steam heated equipment and allows handling of the formed piece at room temperature. This pitch also presents a problem by being thermoplastic as the piece must be carefully supported during subsequent baking to prevent slump of the piece prior to the curing of the binder. Thermosetting binders can be used but here again economic considerations are a major deterrent to their extensive use.

Forming: The prepared mix is formed into shapes by extrusion or molding. Both these forming methods have an effect on the anisotropy of the finished graphite. Particle size, shape and distribution of the calcined coke also have an influence on ordering that occurs during forming. Most cokes used by the industry have particles that have a long dimension; during extrusion forming the long dimension lines up parallel to the direction of extrusion and during molding the long dimension of the coke particles align normal to the molding pressure. The anisotropy induced by raw materials and forming carries through to the graphitized piece.

Baking and Graphitization: During the first heat treatment the formed piece must be carefully supported since the binder again liquifies and the piece becomes plastic. As the binder pyrolyzes large quantities of gases are evolved; therefore heating must be slow during the periods of high gas evolution to allow gases to escape without distorting or breaking the piece. Polymerization and cross linking in the binder and between the binder and the filler occurs as the temperature is raised to 1400-1700°F. After baking the piece may be impregnated with a pitch and baked again if a stronger, more impermeable graphite is desired. In the final heat treatment to 4500-5400°F the remaining volatiles are removed and the carbon is converted to graphite. By the time the temperature has reached approximately 2700°F most of the impurities have been removed and the carbon

piece is composed of small crystallites, of about 30Å in size built of disorganized stacks of parallel planes of condensed benzene rings, in a matrix of a disorganized carbon phase. From 2700°F to final graphitization temperature the crystallites grow, first at the expense of the disorganized phase and then smaller crystallites. Around 3800°F the carbon crystallites have reached the size of about 150Å in the a-direction and begin to change into crystallites of graphite by the rotation and relative shift of layer planes. Continued temperature increase results in a rapid growth of graphite crystallites. Mrozowski (1) suggests that perhaps the main driving force is due to the thermal stresses caused by the anisotropic expansion of the crystallites assisted by energy of the thermal motion. It is also believed that three-dimensional alignment proceeds by the movement of boundaries or arrays of dislocations (2).

Influence of Graphite Structure on Properties

Porosity: Without impregnations the process as described above produces a relatively porous, low density graphite. The porosity of graphite can be divided into two types; 1) pores that are left due to the loss of volatile constituents, and 2) those that are caused by differential contraction of the crystallites. The largest source of pores is between particle voids due to volatile constituents from the binder. This porosity may be decreased by successive impregnations and heat treatments but theoretically these pores cannot be processed out. The latter porosity is referred to by Mrozowski (3) as "unavoidable" porosity. Mrozowski states that even though the polycrystalline graphite should be perfectly dense at the highest heat treatment temperature, voids will be formed as it cools. These voids are caused by differences in contraction along the a- and c-directions of the randomly oriented crystallites. Unavoidable porosity would naturally decrease as the crystallites assumed a preferred orientation and would increase with more random orientation. A dense material (2.25 g/cc) has been obtained by applying very high pressure and temperature to a polycrystalline graphite with original density of 1.9 g/cc (4). The plastic flow produced at high temperature and pressure evidently allowed the crystallites almost to completely align with their c-axis parallel to the compressive force, therefore practically no unavoidable porosity was formed during cooling. Green (5) also suggested this technique as a means of increasing density and strength in graphite. A high density graphite (ZTA grade) developed by the National Carbon Company has been referred to as a "hot-worked recrystallized" graphite, and this description also implies the use of pressure and temperature to produce a high density graphite.

Thermal Properties

Thermal Expansion: Thermal expansion is a very interesting and not well understood property in polycrystalline graphite. The thermal expansion of graphites as temperature is increased shows the net influence of thermal vibrations of the lattice atoms, the elastic properties of the crystallites and the details of bonding and connection between the crystallites and particles consisting of these crystallites (6). The graphite crystallite is extremely anisotropic and as a result large differences in expansion are experienced in directions perpendicular and parallel to the layer planes. The most complete study of the thermal expansion of single crystal graphite was made by Nelson and Riley (7). Measurements were obtained over a range from 60 to 1470°F and extrapolated to higher and lower temperatures by a solid state theory development for the graphite lattice. Their results are shown in figures 2 and 3. These results show that in the c-direction graphite expands with increasing temperature at all temperatures above absolute zero. However, a shrinkage is experienced in the a-direction as the temperature is increased from absolute zero to approximately room temperature. As the temperature is increased further the crystal expands in the a-direction. Figures 2 and 3 also show the range of

expansion coefficients observed in bulk manufactured graphites. The relationship between bulk thermal expansion of manufactured graphites and the single crystal is not well understood. The extreme anisotropy of all properties of the graphite crystal complicates the situation. It is believed that a better understanding of the thermal expansion of polycrystalline graphites will also aid in understanding other properties. Mrozowski (8) has proposed a model for polycrystalline graphite and used it in an explanation of the relationship between single crystal and polycrystalline properties. According to the model, the anisotropic crystallites are joined by strong bonds at the peripheries of the larger planes. The model suggests that when polycrystalline graphite is cooled after heat treatment the strong cross linking of the bonds restrict the contractions of the body due to the low contraction of the crystallites in the direction parallel to the planes. The difference in contraction parallel and perpendicular to the planes causes unavoidable porosity and internal stress build up. Viscous creep relieves the stresses at temperature above 4100-4500°F, however, as the temperature is lowered the stresses are locked in.

Using the same model Collins (9) suggests that as the graphite is reheated the crystallites expand back into created voids thereby contributing little to the overall expansion of the system. This would help to explain some of the difference between the expansion of the crystallites and manufactured graphites.

From a process point of view, many variables affect thermal expansion of a graphite. Differences in coke have the strongest effects and these arise from many variables. Some of the variables are: raw material used in making the coke, various process parameters during coking and calcining, and particle size. These differences are further complicated by the effects of the binder on the coke and other process variables during forming and heat treatment of the graphite (10, 11).

The thermal expansion coefficient of all bulk graphite increases with increasing temperature and although the coefficients for various graphites vary over a wide range, the change in expansion coefficient with temperature is approximately the same for all graphites as shown in figures 2 and 3. As a result of this relationship the mean linear coefficient of the thermal expansion between room temperature and any final temperature can be obtained by adding a predetermined factor to the room temperature to 100°C coefficient.

Thermal Conductivity: In the a-direction the thermal conductivity of a graphite single crystal is probably higher than that of any other material. In the c-direction thermal conductivity is very low. Manufactured graphites are generally considered good thermal conductors; however, thermal conductivity can be varied over a wide range depending on the type of graphite and/or its crystallite orientation. Table 1 gives the thermal conductivity of a number of various graphites and illustrates this range. It is generally accepted that heat transfer in graphite is a lattice vibration mechanism; the decreasing thermal conductivity above room temperature is consistent with this assumption (12). In polycrystalline graphite thermal conductivity is greatly influenced by the size of the crystallites, intercrystallite bonding, orientation effects and porosity. Here again these are influenced by numerous interdependent variables from raw material processing to graphitization which in turn affect the final thermal properties. In manufactured graphites the thermal conductivity of the piece decreases as the temperature increases, as shown in figure 4.

Specific Heat: A review of the literature indicates that specific heat does not vary much from one grade of graphite to another. The specific heat curve of several graphites is summarized in figure 5.

Emissivity: Since the aerospace interest in graphite is primarily in the high temperature range where heat transfer by radiation is dominant, emissivity is an important property. Emissivity varies with different types of graphite and surface finish. Furthermore, even when starting with a polished surface, heating at high temperatures will alter the surface and increase its emissivity. A representative emissivity value for graphite is 0.77 (15). A value of 0.98 has been obtained based on reflectance measurements of the crater of an operating arc (16). It is noted that reflectance measurements yield higher emissivity values than are obtained with an optical pyrometer and the difference is not understood. Another reference stated that the spectral emissivity of graphite near 0.65 wave length is not structure dependent to a high degree and a value of 0.70 to 0.80 can be obtained with polished surfaces, while dull and oxidized surfaces can be as high as 0.98 (17).

From an aerospace standpoint one of the most interesting properties of graphite is its increased strength at high temperatures. For most graphites, strength reaches a maximum at approximately 4500°F and at this temperature, the strength may double the room temperature value. The strength of the majority of the bulk graphite grades drops off rapidly above 4500°F; however, creep data on a recently developed bulk graphite indicates it has a useful strength up to 5000-5500°F range. Mrozowski (18) explained graphite's strength-temperature dependence by attributing it to the relief of "frozen in" stresses which arise from the anisotropic contraction of the individual crystallites in the polycrystalline solid. Martens et al (19) suggested that increased plasticity of graphite at high temperature may permit local deformation around the stress-concentrations and therefore permit higher loads to be sustained before fracture. At temperatures above 4500°F the material is so plastic that changes in temperature do not materially affect flow around the stress concentration and strength decreases with increasing temperature in the manner exhibited by most other materials. Mrozowski (20) also suggested that the failure at high temperatures is of a plastic nature. He suggested that the surface of the fracture gave the appearance of a brittle fracture because failure occurs through the binder bridges or between the binder and the filler particles. Green (21) has offered an alternative interpretation based on the polymeric nature of the inter-crystalline valence bonding. The increase of strength with increasing temperature is shown in figure 6.

Flexural and compressive strengths also increase with increasing temperatures in the same manner as tensile strength. Flexural strengths are easier to measure than tensile strength and are commonly used for control purposes. It should be noted that it is important to state the method of measurement when giving flexural strength as "single point" loading gives a value approximately 20 to 25 percent higher than "third-point" loading (22).

The high temperature creep characteristics of an experimental high density graphite (ZT type) and a conventional grade are shown in figure 7. The low creep rate in its strong direction at 5500°F indicates that structural strength remains at this high temperature. The markedly higher creep with temperature across the grain as compared to along the grain of the ZT graphites indicates a different creep mechanism in the two directions as might be expected. (See figure 8 for sample grain orientation.)

The elastic moduli also increase with temperature up to about 3600°F and decrease after this peak. Hove (23) suggested that the increase is caused by the large c-direction expansion of the crystallites which tend to fill up the intercrystalline voids. This jamming would thus stiffen the structure.

Chemical Properties

Graphite is subject to three types of chemical attack: oxidation, formation of lamellar compounds, and reaction with and solution in carbide-forming metals in certain high temperature ranges. In many aerospace applications oxidation is a serious problem and graphite must be protected from oxidizing atmospheres at high temperatures. Janes (24) studied the effect of a number of raw material and process variables on oxidation resistance and concluded that particle size of the filler component, pore size, and total and type of porosity, type of forming, use of non-graphitizable components, and the use of binders other than coal tar pitch all have only a minor effect on oxidation rate. It was also noted that catalytic impurities have a decided effect on oxidation rate at relatively low temperatures. At high temperatures the oxidation reaction is reported to be diffusion controlled and catalytic impurities have little effect. Since the rate of oxidation is diffusion controlled it is quite responsive to the rate of flow of the oxidizing gas. Pyrolytic graphite is reported to have better oxidation resistance than bulk graphites; however this advantage disappears at high temperatures. At the present, the best high temperature protective coating for graphite is silicon carbide and this coating is limited to a temperature of approximately 3100°F. The protection afforded by this coating is time - temperature dependent so this temperature may be high or low depending upon the application. The major problem associated with present coatings is a mis-match of coefficients of thermal expansion between the substrate graphite and the coating which can cause spalling and cracking of a coating. Optimization of a coating system for graphite for higher temperatures will probably include tailoring the substrate graphite to more closely match the expansion of a coating and from the coating standpoint it appears that a composite coating will evolve which takes advantage of higher melting materials (e.g., oxides, borides, etc.). In this case a diffusion barrier would be necessary to protect the substrate from the higher melting coatings since carbon would react with many of these higher melting materials. Care must be taken not to compromise graphite's high emissivity by the application of a low emissivity coating thereby reducing the total capability of the graphite-coatings composite.

The second type of chemical reactivity is the formation of lamellar compounds. This type of reaction is characterized by the intrusion of various molecules or ions between the layer planes of the graphitic lattice. The formation of lamellar compounds can lead to the destruction of the piece. Graphite also reacts with carbide forming metals at high temperatures. This may be desirable or undesirable depending upon the combination of properties desired.

Thermal Shock Resistance: Since thermal shock resistance is not relatable to any single property but instead a combination of thermal and mechanical properties, it is convenient to treat this property as a separate item. By reducing thermal shock theories to the most significant factors as they effect graphite and most applications, it can be said that thermal shock resistance is directly proportional to tensile strength and conductivity and inversely proportional to Young's Modulus and coefficient of thermal expansion. The high conductivity, low thermal expansion and low modulus of most polycrystalline graphites primarily account for graphite's high thermal shock resistance as compared to other non-metals. It should be noted that the properties that affect thermal shock resistance can be varied in the various types of graphite, and thermal shock resistance can be affected. For an example, in rocket nozzle tests some of the higher density ZT graphites have cracked from thermal stresses.

Erosion: There are a number of factors that influence the erosion of graphite and as a result the exact mechanisms are not well understood. In its simplest terms erosion can be divided into chemical reactivity and mechanical abrasion. As with all chemical kinetics, other factors being equal, the rate of attack will increase with temperature. For use in the earth's atmosphere at high temperatures, oxidation is the major factor and as mentioned previously, graphite must be protected from oxidizing environments. In rocket nozzle applications, chemical and mechanical effects are magnified and complicated by the higher temperatures, pressures and velocity of the exhaust gases. In addition to the oxidizing effect (if present), other constituents in the exhaust gases may have a serious effect on the chemical reactivity of graphite. Impurities already present in the graphite are also believed to affect the mechanisms involved. A microscopic study of bulk graphites after exposure in a rocket motor reveals that attack occurs preferentially in the binder material. The particles thus weakened by the loss of the binder are then more susceptible to mechanical erosion. On a crystallite scale, attack is not on the basal planes, which are bonded by strong bonds but primarily on their edges. From this, one could conclude that the most beneficial structure at the exposed surface is a highly orientated structure with the basal planes exposed. Pyrolytic graphite rocket nozzle tests confirm this effect. On the other hand, nozzle inserts of a high density highly orientated bulk graphite (Grade ZTA) tested with the orientation so that more edges than basal surfaces are exposed, have also performed quite well. One can only conclude that the mechanism of erosion is quite complicated and not well understood. However it is apparent that microstructural detail, external environment, and the thermal, mechanical and chemical properties all affect erosion. A detailed understanding of the combined effects of these factors is in its infancy.

Requirements for Graphite in Aerospace Application

The full realization of drawing board capabilities is limited by the lack of suitable materials to cope with the severe environmental conditions of aerospace flight. Future progress in the aerospace realm largely depends upon improved materials that will endure these extreme environments. Of course the optimum aerospace material would have an extreme melting point, high strength, high thermal and mechanical shock resistance, and zero density. Unfortunately such a material does not exist. Materials that look good from the high melting point consideration have other detrimental properties, e.g. low strength, low thermal shock resistance. The aerospace materials problem represents a formidable challenge for both the designer and the materials developer. So that this challenge may be better understood where graphitic materials are concerned several of the more demanding materials applications will be discussed.

From a propulsion standpoint aerospace vehicles, at the present and in the foreseeable future, will depend upon some form of rocketry for the higher speeds and greater load carrying capabilities which are needed. The greater thrust required to achieve these capabilities can be obtained by simple scale up or more efficiently by higher energy fuel. These new fuels and greater thrust mean higher temperatures, higher pressures, greater total heat flux and in most cases a more corrosive environment.

From the vehicle structure standpoint, specific flight profiles must be considered as each profile presents different problems. For a ballistic type vehicle the nose cone experiences the most severe thermal environment. Its re-entry is characterized by extremely high temperatures for a short period of time. The optimization of the ballistic re-entry profile necessitates higher ground approach speeds to increase accuracy and lessen the possibility of interception. Nose cones incorporating graphite (pyrolytic graphite on a composite graphite system) offer interesting potential in this materials application.

Graphite's high emissivity and high temperature capability present some interesting advantages. Generally speaking, all graphites have these advantages but most are ruled out because of high conductivity. However, by controlling crystallite orientation and in some cases other properties, graphite can become a good high temperature insulator as in the case of pyrolytic graphite and some forms of bulk graphite. A glide re-entry is characterized by lower temperatures than ballistic re-entry and longer exposure to the earth's atmosphere. Whereas oxidation resistance is a minor factor in ballistic re-entry, it is a major concern for longer periods in oxidizing environments. Mechanical properties are somewhat more important in this type of application, but structures can be designed that will have the major load transmitted to stronger, thermally protected members of the structure. The addition of a man to these vehicles increases the reliability requirements and also of the materials. The materials applications mentioned above are probably the most challenging ones facing the materials developer and vehicle designer in this new era of aerospace vehicle development; however, the challenges are not insurmountable. Of the various materials possibilities, graphites in one form or another, or in combination with other materials, are outstanding candidates to meet the challenge.

The more exotic applications suggested above by no means constitute a limit of materials applications where graphites should be considered as candidates in aerospace designs. Graphites are a family of materials with the capability of being tailored to meet a large variety of high temperature applications. On a density scale this family extends from foams on the low side to high density bulk graphite and pyrolytic graphite approaching the theoretical density of 2.26 g/cc. It should be noted that even these high density graphites are in the same weight class as aluminum. As a result of its light weight and the importance of weight in aerospace vehicles, various forms of graphite also have the potential of being competitive in temperature ranges not normally associated with graphite. Table 2 illustrates the range of properties available in various forms of graphite. Graphite can be a thermal insulator or a conductor and the strength of various graphites vary over a wide range. It is also seen that there are limits to tailoring all the desirable properties of graphite into a single piece. The fibrous materials, yarn and felt, could be used in fibrous form or in composite materials such as the cloth laminate type. Single crystal and whisker properties are given only to indicate a property limit in the material and do not constitute a useful form.

The requirement for a more uniform and reproducible graphite product has long been a challenge to the graphite industry. New graphite technology has made significant progress in this area. Feasibility of reducing the variability of properties by at least one-third that of presently accepted missile grade graphite (in comparable sizes) has been proven. The processes involved also have the capability of scale-up so that higher quality graphites of the conventional bulk variety have the potential of being available in larger sizes. However, the day on which pieces fifty inches in diameter with properties equal to even present ATJ graphite is not in the foreseeable future.

Another major challenge and aerospace requirements is for oxidation resistant materials in the temperature range above 2900°F. A great deal of work has been done on developing coatings for graphite; but in useful shapes and sizes, most have had only limited success in the higher temperature range. As stated previously, failure is primarily due to the differences in thermal expansion of the coating and the substrate. Graphite substrates with higher expansion coefficients offer good potential in reducing this challenge. Coating materials with higher temperature capability than the best available siliconized coatings are available. Practical coating systems and experience with them in practical application has not yet been accomplished.

Summary

From a basic science standpoint it can be said that there are many areas where fundamental knowledge is inadequate. The classical approach to studying a material through single crystals is limited in the case of graphite by the difficulty of obtaining reasonably large crystals and the inability to account for the lack of correlation between single crystal and polycrystalline studies. The study of polycrystalline graphites has had an empirical approach for the most part and has been limited seriously by competitive considerations within the industry. It should also be mentioned that these competitive considerations have restricted the publication of the majority of the work done within the industry.

To obtain a better understanding of the industry and the graphite situation there are several things to be recognized: First, over the years the graphite industry cornered most of the graphite knowledge and skills, and proprietary secrecy hangs heavy over most of the industry's efforts, particularly work concerning fabrication technology. And second, this industry is a highly competitive one, with most of its resources directed to markets where commercial incentive was the greatest. Aerospace applications constitute only a very small fraction of the commercial market and demand much of graphite in terms of properties. Outside the industry very little work has been done on graphite until recent years, partly due to the need for specialized equipment.

When the time came to use graphite in aerospace designs, it was necessary to choose off the shelf items since there was no other choice; however, the need for greater reliability as an engineering material, and more severe environments, demanded improved materials. Therefore, various competitive factors, and a stimulated interest in graphite, required that major advances be made in graphite technology. New techniques that are in many ways revolutionary to graphite technology, are being developed and consequently the family of graphitic materials has been enlarged and improved. The variety of properties available in graphites is evidence that such a material can and should be tailored for specific aerospace materials applications. It is also clear that graphite is a material of great importance to high temperature aerospace technology and will find increased use in advanced systems.

REFERENCES

1. S. Mrozowski, Proc. 1st and 2nd Carbon Conf. Univ of Buffalo (1956) p.37.
2. S. Mizushima, Proc. 4th Carbon Conf. Pergamon Press, (1960) p. 420.
3. S. Mrozowski, op. cit., p.34.
4. P.W. Bridgman, J. Chem. Phys. 15, 92 (1947).
5. L. Green, J. App. Mech. 20, 2 (1953) p. 294.
6. "Research and Development on Advanced Graphite Materials" WADD TN 61-18 p. 40.
7. J.B. Nelson and D.P. Riley, Proc. Phys. Soc. (London), 57, (1945) p. 477-95.
8. S. Mrozowski, op. cit. p. 33.
9. F.M. Collins, Proc. 3rd Carbon Conf. Pergamon Press (1959) p. 656-74.
10. J. Okada, Proc. 4th Carbon Conf. Pergamon Press, (1960) p. 553-58.
11. F.M. Collins, op. cit.
12. L.M. Currie, V.C. Hamister, H.G. MacPherson, "The Production and Properties of Graphite for Reactors", Paper presented at UN International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955.
13. S. Mrozowski, Proc. 1st and 2nd Carbon Conf. p. 155-166.
14. J.E. Hove, Proc. of 3rd Carbon Conf. Pergamon Press, (1959) p. 515-527.
15. Industrial Graphite Engineering Handbook, National Carbon Company.
16. W.W. Lozier, "Development of Graphite and Graphite Base Multicomponent Materials for High Temperature Service", WADD TR 59-789, April 1960.
17. "Report of the Ad Hoc Committee on Refractory Inorganic Nonmetallic Structural Materials", MAB Report 169-M, January 1961.
18. S. Mrozowski, op. cit. p. 31.
19. H.E. Marters, L.D. Jaffe, J.E. Jepson, Proc. 3rd Carbon Conf. Pergamon Press, (1959) p. 529.
20. S. Mrozowski, op. cit. p. 44.
21. L. Green, Proc. 4th Carbon Conf., Pergamon Press, (1960) p. 497-509.

REFERENCES (Cont'd)

22. L.M. Currie, V.C. Homister, H.G. MacPherson, op. cit.
23. J.E. Hove, Trans. Metall. Soc. AIME TP 2622E, February 1958.
24. M. Janes, "Graphite-Based Materials for High Temperature Applications", WADC TR 57-602, February 1958.

GRAPHITE CRYSTAL LATTICE

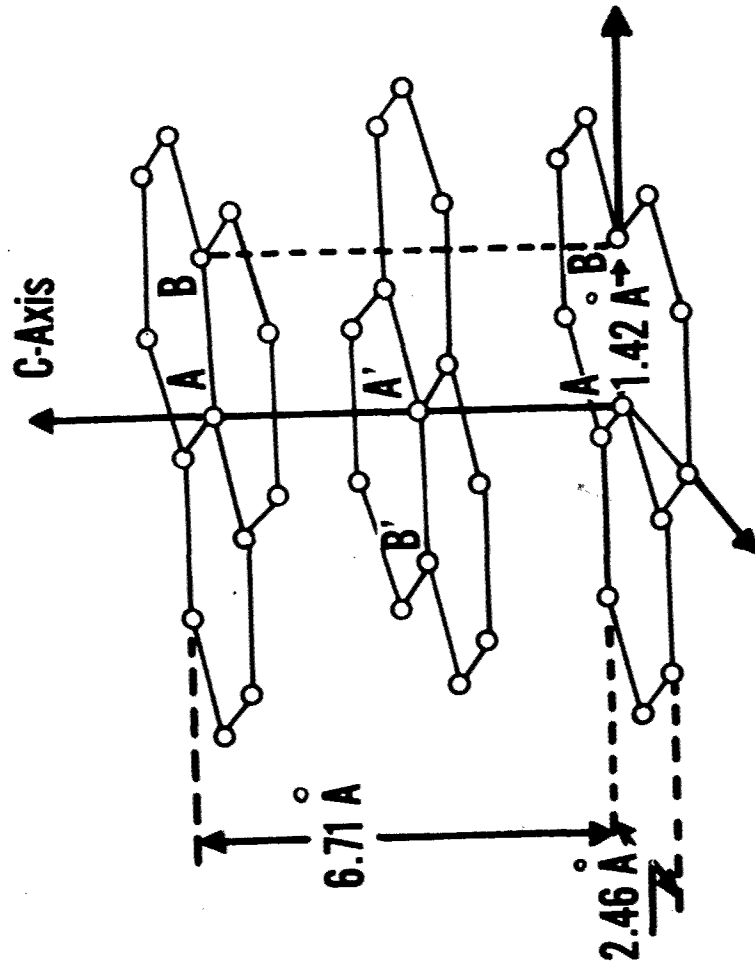


Figure 1. Structure of Graphite

THERMAL EXPANSION OF GRAPHITES

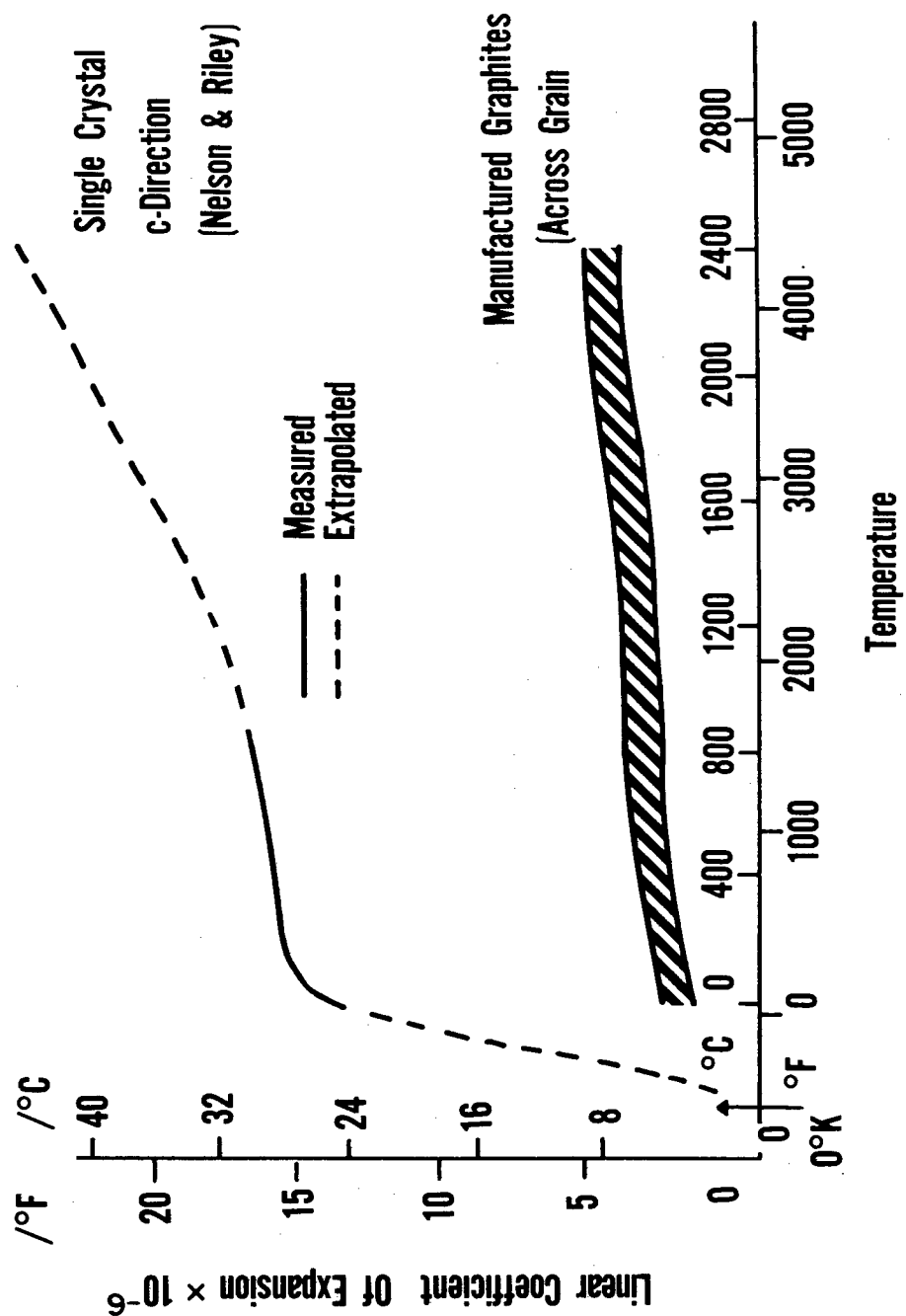


Figure 2. Thermal Expansion

THERMAL EXPANSION OF GRAPHITES

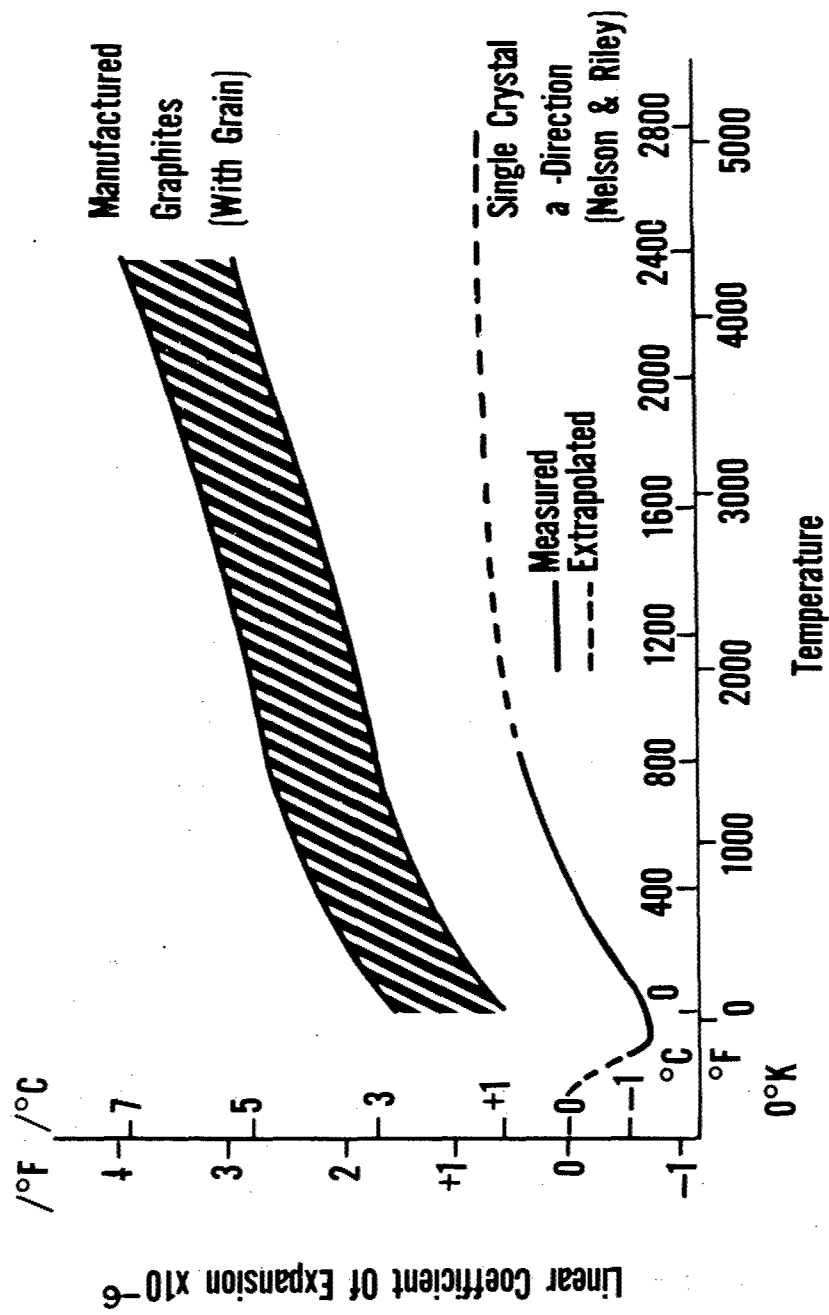


Figure 3. Thermal Expansion

THERMAL CONDUCTIVITY OF ATJ GRAPHITE

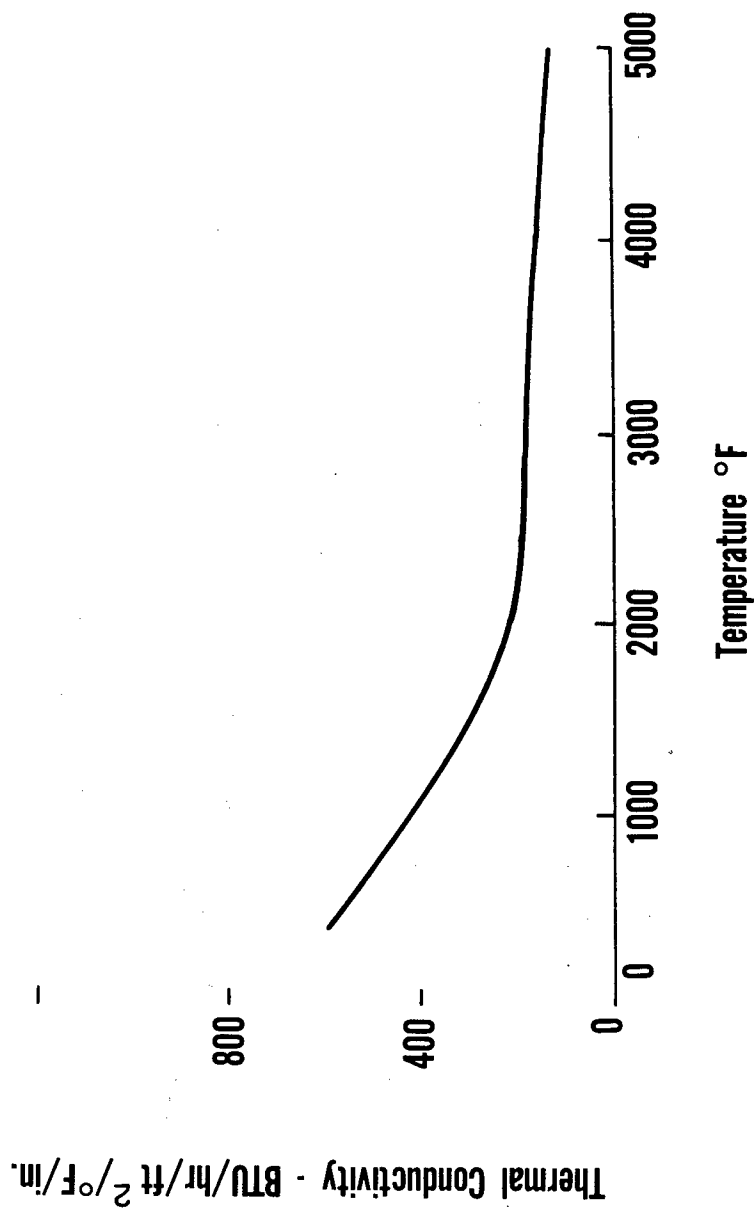


Figure 4. Thermal Conductivity vs ATJ Graphite

SPECIFIC HEAT OF FOUR GRAPHITES

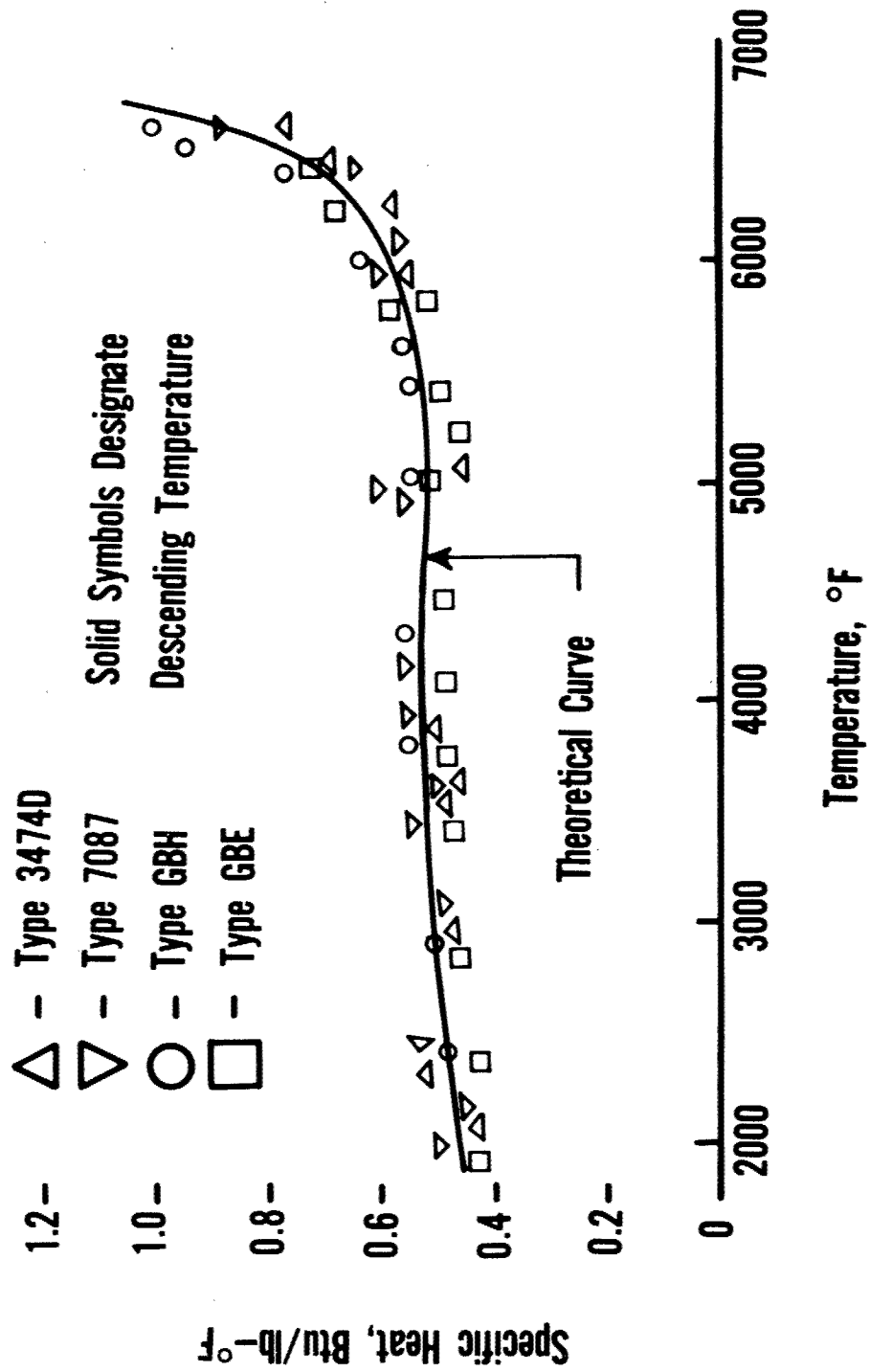


Figure 5. Specific Heat of Graphite

TENSILE STRENGTH vs. TEMPERATURE (Parallel To Grain)

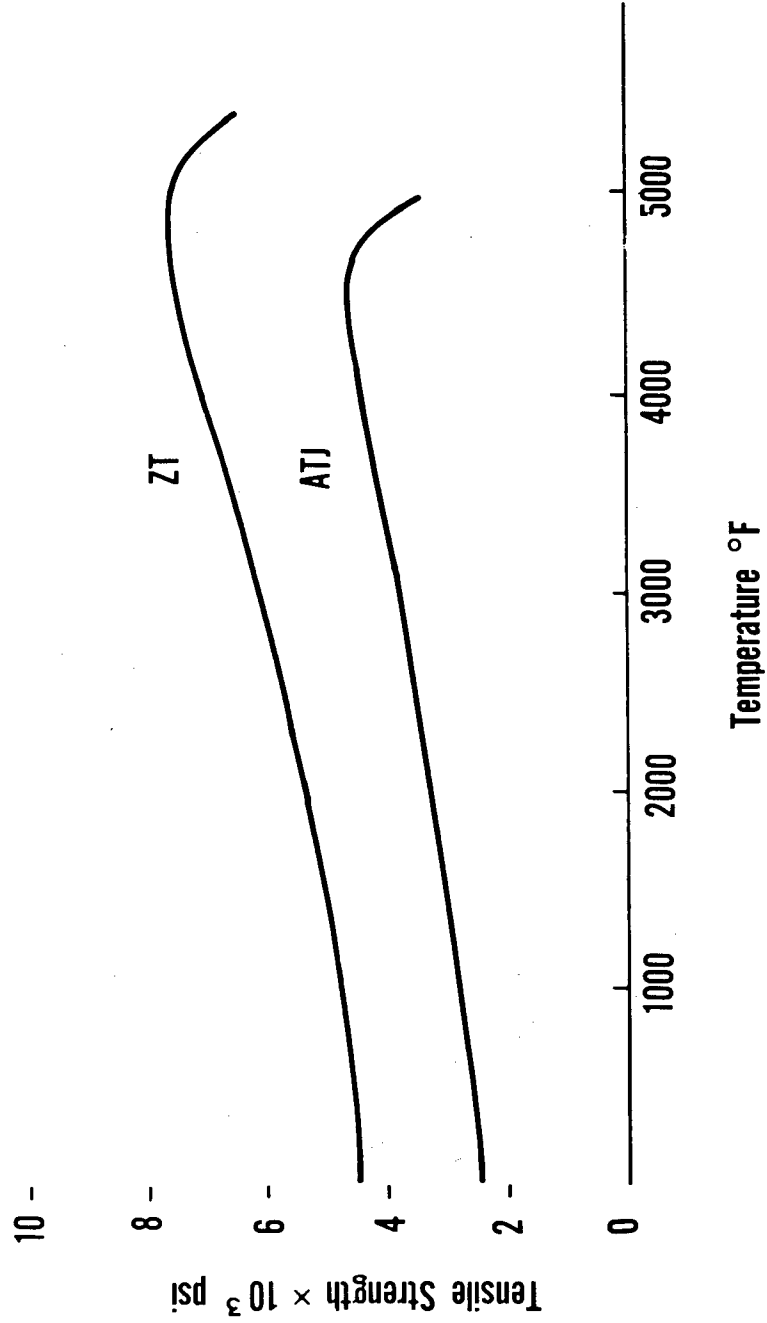


Figure 6. Strength vs Temperature

CREEP OF ZT AND ATJ GRAPHITES

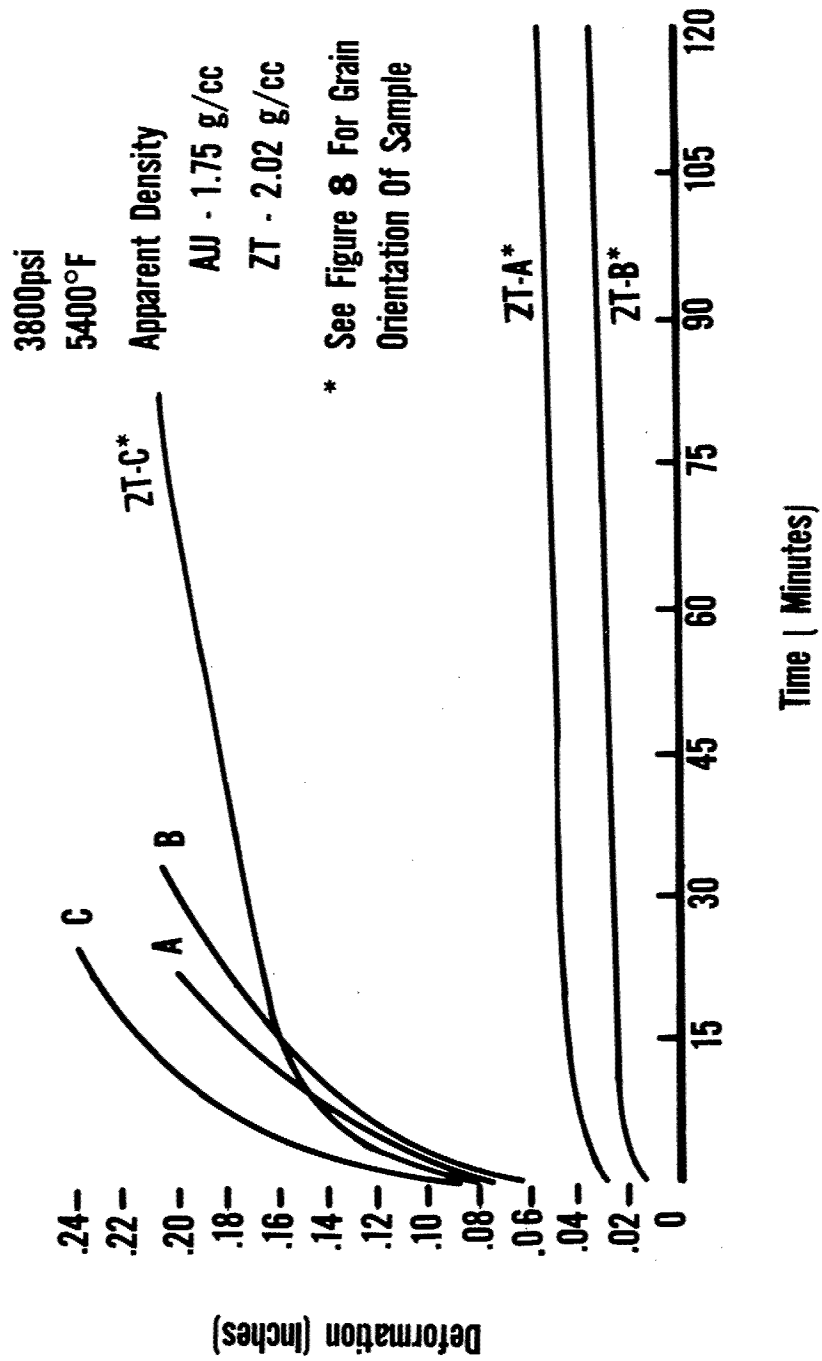


Figure 7. Creep of ZT and ATJ Graphite

GRAIN ORIENTATION FOR CREEP SAMPLES

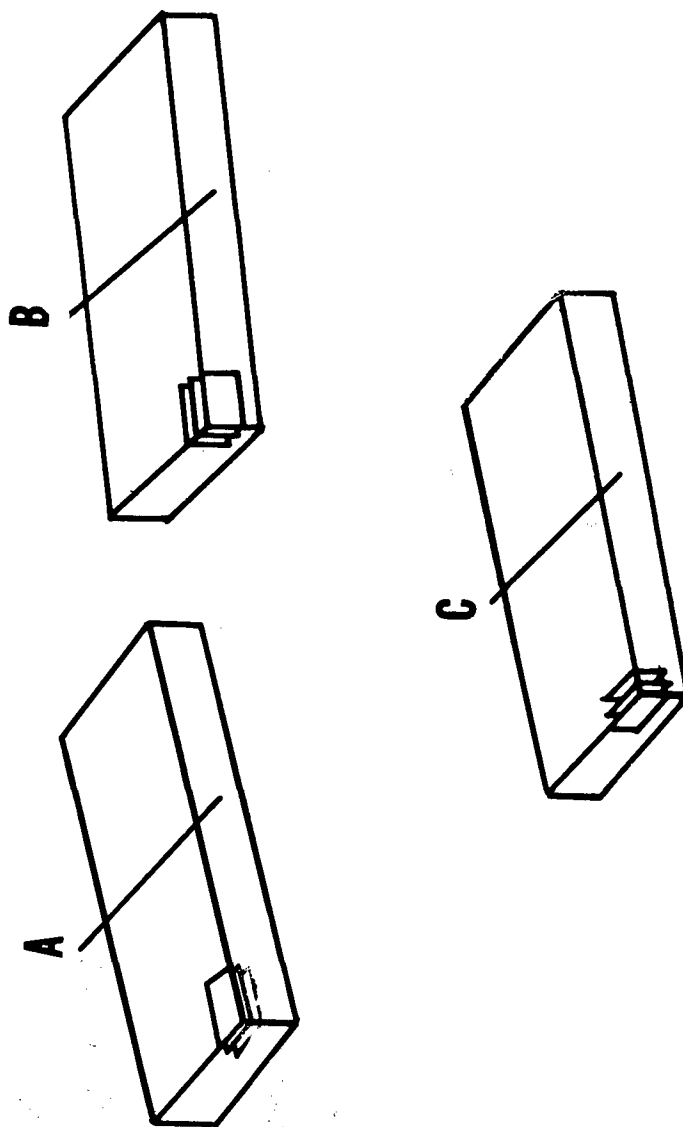


Figure 8. Grain Orientation of Creep Specimens

Table 1

THERMAL CONDUCTIVITY OF GRAPHITES

Room Temperature Conductivity
(BTU/ft. hr. °F)

	WITH GRAIN	ACROSS GRAIN
Graphite Crystal	800	
Pyrolytic Graphite	200	0.8
ZT Graphite	150	40
ATJ Graphite *	44	36
Graphite Cloth Laminate	1.2	.9
Graphite Foam	0.5	

* ATJ Graphite Is A Commercially Available High Quality Product Of The National Carbon Company

Which Has Become Widely Recognized As A Point Of Reference When Comparing Graphites.

For This Reason Extensive Use Of ATJ Characteristics Has Been Made

For The Convenience Of The Reader.

Table 2

PROPERTIES OF A NUMBER OF GRAPHITES

GRAPHITES	THERMAL PROPERTIES		MECHANICAL PROPERTIES	
	CONDUCTIVITY $\frac{W^3}{A^4}$	CTE $\frac{W^3}{A^4}$	TENSILE STR. $\frac{W^3}{A^4}$	MODULUS $\frac{W^3}{A^4}$
Foam	0.5	0.5	Fiber Strength 46,000 psi	1.15
Yarn				
Felt	0.2			
Cloth Laminate	1.2			
ATJ	65	3.6	1700	1.40
ZTA	85	0.8	5000	2.4
Pyrolytic	200	-1.0	27.0	9.0
Single Crystal	800		300,000,000	100
Whiskers				

● BTU/Ft. Hr. °F/Ft.

● Coefficient Of Thermal Expansion $\times 10^{-6}$ /°C. (0 To 1000°C)

● With Grain

● Across Grain

● Tensile Strength psi (Room Temperature)

● Elastic Modulus $\times 10^6$ psi

PLASTICS, ADHESIVES AND COMPOSITE MATERIALS

Chairman

Mr. R.C. Tomashot

Speaker

G.P. Peterson

Panel Members

Mr. F.W. Kuhn

Mr. J. Rhodehammel
(Edwards AFB)

Dr. G.F.L. Ehlers

Mr. F.H. Bair

PLASTICS, ADHESIVES, AND COMPOSITE MATERIALS

F.W. Kuhn

G.P. Peterson

R.C. Tomashot

Directorate of Materials and Processes, ASD

Introduction

The first large scale application of reinforced plastic materials in aircraft occurred almost twenty years ago when polyester resin laminates were used in radomes. The materials selection at that time was primarily based upon the required electrical transparency of such a material. For this particular application, the electrical properties continued to be highly important, but in addition the continued success in efforts to improve the structural efficiency of reinforced plastics has resulted in recognition and present use because of structural advantages over other materials. Research on metal to metal adhesives has also been successful to the point that these materials have in many cases moved from the category of secondary structure bonding to their use in primary flight vehicle structures. Further improvement in the structural capability of materials of this type is indicated and forms the basis for the current and planned materials research on nonmetallic composite materials. While this may narrow the scope to such types as reinforced plastics and high performance adhesives for bonding structural materials, it also at the same time brings in necessary consideration of many other types of materials. For instance, since reinforced plastics are actually a composite of reinforcement and binder, integrally related research effort must be expended on both the reinforcement member and the binder to obtain the highest possible improvement. A further important consideration concerns the process by which the component materials are combined into a completed structural unit, since this can have a pronounced effect upon final properties and material capability.

Discussion

The format for the discussion to follow comprises the state of the art and research efforts according to individual material components, uses, and composite processes.

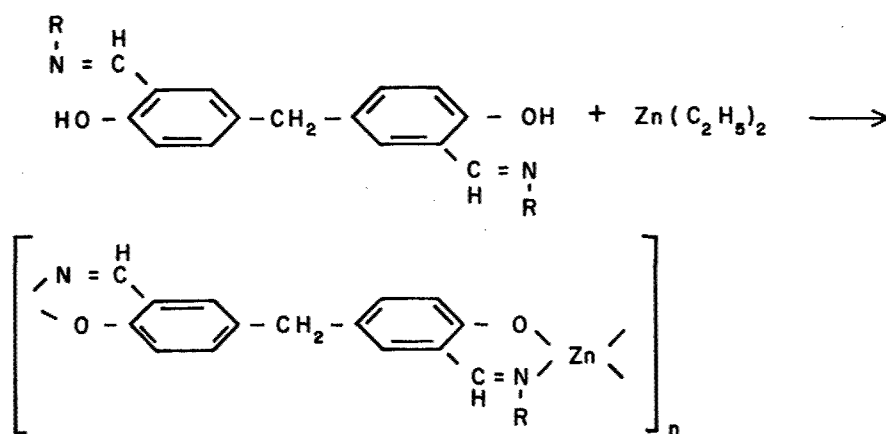
Broadened effort to obtain radically improved reinforced composites has expanded the category of materials formerly referred to as laminating resins to what may generally be called matrix materials. Laminating resins are still an important sub-category, but so are any other materials possessing the specific properties which will enable it to perform a load transfer function within the composite.

Laminating resins based upon high polymeric materials have received by far the most attention in the effort to obtain new and improved matrix materials. Progressive development has proceeded from original polyester formulations to the silicone-modified phenolic resins representing the latest completed development. While other advantageous features have been obtained such as reliability and ease of processing, the principal Air Force endeavor in all of its resin research has been directed toward improved high temperature capability. As a result of this research, the present capability in laminating resins is around 500°F for conditions of long time exposure, and up to 700°F for shorter periods of time.

Improvement beyond the 500°F temperature has been difficult for long time exposure. The silicone and silicone modified phenolic resins can provide usable strength to 700°F depending upon the time and temperature, but generally not to exceed a few hours at 700°F.

To obtain long time thermal stability at 700°F and above, new and radically different approaches must be investigated. One general approach is the utilization of unique organic, semi-organic, and inorganic polymers having outstanding thermal stability. To obtain high molecular weight polymers of these types a great deal of research is underway and will include modification of some of the advanced polymer types to provide the required mechanical and adhesion characteristics.

An example of a specific type under study is the chelate coordination polymer. Its selection was based on the observation that in many instances its coordination with metals induces temperature stability in the polymer. This has indeed been true with a polymer formed through the reaction of methylene-bis-salicylaldehyde with diethyl zinc in pyridine solvent:



However, to be useful as a laminating resin, other characteristics must be favorable. Of these, two characteristics which have not been satisfactorily achieved as yet in this type polymer are molecular weight and extensibility or toughness, and it appears that the two properties are quite closely related. Molecular weights on the order of 10,000 have been obtained. However, it has been tentatively concluded that for a polymer system containing such rigid segments a molecular weight of at least 40,000 to 60,000 must be obtained in the linear polymer, before crosslinking, to insure good mechanical toughness. Efforts at the present time are being concentrated on means of obtaining this minimum molecular weight. However it is significant that even with the low molecular weight polymer, it has been possible to prepare a reinforced laminate. The laminate is of low strength, but to our knowledge, this is the first chelate polymer from which any laminate could be prepared.

Similar efforts are underway on a borazole resin which, because of its ring structures of alternate boron and nitrogen atoms, possesses thermal stability above 800°F.

Another approach under study which may generally circumvent the low molecular weight problem of the inorganic or semi-inorganic polymers is that of converting high molecular weight organic polymers to semi-organic polymers of high molecular weight. In many heat resistant polymeric systems already available, it has been demonstrated that in most cases it is thermally weak linkages which produce premature oxidative degradation. The methylene bridges in phenolic resins are a case in point. If these

bridges can be replaced by reactive inorganic groups it may be possible to obtain high molecular weight inorganic polymers of resinous materials which will also possess good mechanical and thermal characteristics.

For extended time temperature capability above 1000°F, it is unlikely that these new polymers, if successful, will perform satisfactorily. More promising, however, is another approach under investigation which is producing some interesting results based on a system of phosphate bonded oxides or what may generally be called chemical reaction cements. The potential of such materials is very good, since by chemical reaction at low temperatures it is possible to form a matrix material thermally stable above 2000°F. This approach may appear to be quite similar to other programs on fiber reinforced ceramics. However, in ceramic materials with their very high elastic moduli and low elongation, it is not possible to realize in the composite the high tensile strength of presently available fibrous bodies. Those mentioned showed elastic moduli of less than 500,000 psi, bending strength up to 3,000 psi, and total deformation approaching 1.0 percent when tested at elevated temperatures of interest. A typical load-deformation curve and composition for one of these experimental inorganic matrix materials is shown in figure 1. Incorporation of a suitable fiber into such a matrix could provide a composite with strengths of several hundred thousand psi. Most of these acid phosphates are extremely corrosive when in contact with glass fibers, and this has prevented an early realization of such composites. Work is continuing on protective coatings from fibers and development of less corrosive matrix materials of this type.

The mention of a "suitable reinforcement" introduces another component material which is receiving vigorous and diversified research to obtain significantly improved properties in structural composites.

Recently completed research concentrated on vitreous materials which could possibly be fiberized, and an exhaustive study was made on both compositions and fiber forming techniques. Two distinct improvements were desired: (1) a significant increase in the fiber modulus of elasticity and (2) improved strength and modulus at elevated temperature.

Toward the former requirement, a successful research program provided YM 31A, which is basically a silica-based glass composition, but containing approximately 12 percent beryllium oxide. This glass can be fiberized in the same manner as conventional "E" glass, has at least equivalent strength properties and chemical resistance, and about 50 percent increase in modulus of elasticity. The improvement in fiber properties has been realized in the laminate (figures 2 and 3).

Improvement in fiber strength at elevated temperature has also been obtained to a lesser extent by several new glass compositions. The fiber tensile strength of two of these new glasses as compared to "E" glass at elevated temperatures is shown in figure 4. Further exploratory research has indicated that the elevated temperature strength may be significantly increased by both inorganic coatings on the fiber and improvement in fiber forming techniques. Studies to achieve the maximum from both of these factors are presently being conducted.

Within the last year specific programs have also started on radically new and different reinforcements for composites. The very high strength obtainable in materials of small cross-sectional area such as whiskers has been known for some time. Also, there are some materials which possess outstanding physical properties, even in bulk form, and would have very great potential if the materials could be obtained in a form suitable for composite reinforcement. Examples of such materials are beryllia, alumina, elemental

boron, and boron carbides and nitrides. Preliminary research has shown that fibrous forms can be obtained from these materials. The particular problems have been homogeneity and sufficient length. There is no theoretical reason why both of these factors cannot be achieved. Furthermore, it should be remembered that other forms of reinforcement can be utilized, such as the glass flake reinforced laminates already developed. The importance of considering a material such as boron for reinforcement is evident from its fundamental properties. Amorphous boron, for instance, with a specific gravity of 2.4, tensile strength of 350,000 psi, modulus of elasticity of 64×10^6 psi, and a melting point of over 3600°F could provide a structural composite material with a specific modulus of 25 million psi if effectively used as a reinforcement. Also, the high modulus of elasticity of such a reinforcement will allow the use of higher modulus, very high temperature-resistant, inorganic-matrix materials of the type previously mentioned.

As noted earlier, a review of composite materials must also include consideration of the process by which the component materials are combined into the completed composite. These fabrication procedures and processes have, in general, been satisfactorily developed by straightforward engineering concepts to take best advantage of the new and improved component materials. One exception, which could contribute outstanding improvement in efficient and unique utilization of the component materials, is filament winding. This type of materials construction has the following major attributes: (1) optimum utilization of the high tensile strength of the reinforcement fibers by orientation so that the fibers carry the bulk of the stresses and (2) process and fabrication variables which can be closely controlled so that uniform and reproducible structures are obtained. The fabrication procedure is applicable to surfaces of revolution and does not complicate fabrication of even the largest structural items. The process basically involves the controlled placement of resin impregnated reinforcements under tension on a mandrel of the desired shape. The success of this fabrication procedure is largely dependent on the properties of the component materials and the process interrelationships which effect the properties of the component materials as they are applied to the mandrel.

The potential of this process has been demonstrated in the fabrication of rocket motor cases in current weapons systems when the ultimate in strength to weight properties is desired. Further research in the area of filament wound composites will provide even greater capabilities. Two of the most critical areas involve the reinforcement and matrix materials, which have already been discussed. In addition, research is required on the design of the composite structure (winding pattern or fiber orientation) and processing or fabrication techniques.

Research efforts have already been devoted toward obtaining optimum matrix materials for use on filament wound composites at temperatures of 750°F, analysis and optimization of process parameters utilized in filament winding, and obtaining meaningful procedures for defining the basic mechanical properties of filament wound composites. New epoxy-novolak resins are suitable for use at 750°F for filament-wound composites — a substantial improvement over previously available filament winding resins, which were satisfactory for temperatures up to approximately 300°F. The inherent materials and process variables were studied to determine which of these parameters are important. These were then closely analyzed and improved so that the most satisfactory filament wound composites, from a strength to weight ratio aspect, could be provided. The program provided initial data which indicated that the amount of tension, evenness of tension, and packing of the reinforcement are the most important parameters. Optimum levels for each of these parameters were ascertained and filament wound composites obtained which enabled 350,000 psi in the glass to be achieved before failure. Meaningful and reproducible

procedures for defining the significant basic mechanical properties of filament wound constructions were also obtained under this program. Optimum specimens and procedures were designed to give an accurate indication of the properties of filament wound composites. These procedures include properties such as hydrostatic burst, hoop tensile, longitudinal tensile, axial compression, interlaminar shear, and flexure. These techniques, procedures, and concepts have been obtained to solve one of the most significant problem areas presently existing in the filament wound composite area. Successful implementation of these procedures will eliminate the present confusion and lack of knowledge in regard to the properties of filament wound composites so that the designers can be provided with accurate data which can be most efficiently translated into end item design.

The successful completion of this program has clearly indicated one of the most critical problem areas, that of winding patterns. Parameters which must receive special attention are end closure design, length/diameter ratio, size and shape of openings in the pressure vessel, wall thickness/diameter ratio, longitudinal-circumferential winding vs helical winding, etc. A program is being conducted on a theoretical stress analysis and experimental data basis which will provide optimum solutions and concepts to be obtained for the highest strength to weight ratio filament wound composites. Figure 5 gives the level of properties presently being obtained with available materials and processes along with an indication of possible improvement.

The assembly of metal airframe structural components with adhesives instead of rivets, bolts, and other mechanical fasteners has many performance advantages in points of strength, stiffness, economy, weight saving, aerodynamic smoothness, fatigue resistance, and damping, as well as certain production advantages in permitting fewer parts and fewer operations.

The first design acceptance of the concept of bonding metal airframe parts together came with the advent of metal helicopter rotor blades. The lifetime of adhesive-bonded aluminum blades was increased several hundred percent over that of aluminum blades assembled with rivets, welds, and bolts. The difference was in the ability of the adhesive-bonded blades to withstand the severe fatigue caused by repetitive alternating bending moments and stresses during flight. Adhesive bonding permits the joining of areas instead of points, thus permitting a gradual transfer of the load from one member to the next by eliminating the stress risers such as the holes of bolted or riveted joints.

Further impetus to the use of adhesives came shortly thereafter with the introduction of sandwich construction which for the purposes of this discussion is defined as a low-density honeycomb-type core bonded to and between two high-density, high-strength face sheets. Sandwich constructions exhibit higher strength per weight ratios than any other type of assembly. There are no protruding rivet heads to disrupt aerodynamic smoothness. A bonded sandwich will flex or bend as a single unit. The skin is provided almost continuous support by the core cell walls.

It was largely because of the advantages offered by adhesive-bonded sandwich constructions and adhesive bonding in general that aircraft performances have advanced to the degree that they have. At the same time, however, it is ironical to note that the same high speed capabilities which these developments helped to create, through lowered weights, increased strengths, improved fatigue resistance, aerodynamic smoothness, simplified design, etc., are now imposing limitations on their continued use. Adding to the increasing temperatures imposed by aerodynamic heating at the higher speeds are the higher temperatures imposed by modern engines.

Although organic adhesives of various chemical types with heat resistant capabilities up to 300°F served well in the fabrication of aluminum airframe structures, the introduction of high performance flight vehicles and the associated increases in temperature resistance requirements have dictated the use of metals of higher and higher temperature resistance and a need for adhesives of equivalent heat resistant capabilities. While modified organic adhesives have been developed for bonding stainless steels into structural components of adequate strength for short time exposures to temperatures in the order of 500° to 600°F, the thermal capabilities of these adhesives are still far below those of the metals and appear to be nearly the ultimate that may be expected from purely organic materials. Brazing and welding have further increased operating temperatures but these are expensive and tedious operations which are difficult to control. Also, brazing alloys necessarily have softening points lower than those of the adherend metals and thus limit the thermal and strength capabilities of the structure to those of the joint. Although inorganic ceramic type adhesive-bonded joints of stainless steels have been developed capable of withstanding tensile loads of several thousand psi at temperatures up to 1000°F, they have exhibited an inherent objectionable property of brittleness. In addition, constantly changing concepts of supersonic speed and space travel are extending the elevated temperature resistance requirements beyond the capabilities of even the stainless steels, and likewise those of available adhesives, into ranges to 2500°F and above.

While nickel or cobalt based metal alloys and refractory metals hold promise of satisfying the requirements for metals of such ranges of temperature resistance, adhesives of equivalent capabilities remain to be developed. Current Air Force research programs are predominantly targeted on such objectives. That the ultimate thermal and strength properties to be expected from organic adhesives will fall short of meeting the advancing requirements seems to be evidenced by three significant facts.

First, commercial resin and adhesive manufacturers who contributed well of their skills, facilities, and capital in developing the first adhesives adopted for military use have failed to qualify a single adhesive under a now 6-year old specification. The principal target requirement of 1000 psi tensile lap-shear strength at 500°F after 192 hours exposure to 500°F in itself is but a token requirement in comparison to the existing and future requirements for stable bonding materials at temperatures upward to 2500°F and for longer periods of time.

Second, although contractual programs for modifying organic adhesives with inorganic additions have succeeded in extending the 8-day thermal stability to 600°F, the resultant initial and elevated temperature strengths have been materially reduced. The first best so-modified adhesive was an epoxide-phenolic resin based adhesive, modified with a silicone resin. Although the silicone resin contributed to the thermal stability of the composite adhesive, the thermoplastic property of silicones in general was reflected in substantially reduced strength of the composite bond at elevated temperatures. Further but still limited progress was made in a research program based on the heat stabilizing effects of various metallic oxides on organic resins. Since organic adhesives of normally poor elevated temperature strengths were found to retain substantial percentages of their room temperature strengths even at elevated temperatures if heated in an inert nonoxidizing atmosphere such as nitrogen, it was theorized that the addition of antioxidants to the adhesives would respond in like manner. This program resulted in an adhesive which displayed a tensile lap-shear strength of 1000 psi at 600°F after 10 minutes exposure to 600°F and 750 psi at 600°F after 8 days of exposure at 600°F. This was an epoxy novolac modified silicone-phenolic heat stabilized with arsenic pentoxide. The state of the art for organic adhesives, in view of these recent developments, can be summarized as shown on the next two figures (figures 6 and 7).

Also, although programs of basic research to synthesize new chemical types of thermally stable organic resins specifically for use in structural metal to metal adhesives have succeeded to the extent of producing resins having in themselves high softening points (above 700°F), to date adhesives based thereon have exhibited poor mechanical strength even to exposures of only 400°F, even though displaying acceptable strengths at room temperature. The most promising candidate materials in these investigations have been polyisocyanurate polymers in which the heterocyclic ring consists of alternate carbon and nitrogen atoms. Investigations to improve the adhesive and elevated temperature strength properties of these polymers are based on the incorporation of controlled amounts of free isocyanate groups in the polyisocyanurate molecule and by attaching phenolic groups to the polymer chain. Progress in this field has however not been particularly significant.

In realization of the obvious impending need for structural adhesive systems capable of bridging the gap between the limited thermal properties of organic materials and the higher thermal capabilities of structural metals other than aluminum, early attention was focused on vitreous and ceramic materials. Based on certain available background information in the field of vitreous enamels and porcelains, preliminary investigations were centered on three general types of compositions, the ceramic-oxide glassy-bonds, the cermets, and the air-setting varieties. The glassy-bond types were found to be superior to the others, particularly in such properties as elevated temperature stability, adhesive strength, low moisture sensitivity, and suitable firing and maturing temperatures, as related to the heat-treating requirements and thermal expansion properties of the adherend metals, and have been the basic structure in succeeding investigations.

A relatively simple ceramic-oxide type adhesive frit is one composed of silicon dioxide, sodium monoxide, and boron oxide obtained by melting together, respectively, raw quartz, sodium nitrate, and boric acid, quenching the resultant molten glass into water (which shatters it and makes it easier to grind in a subsequent ball-milling operation), drying, and then milling to a desired fineness. Each of the above oxide-frit components contributes a particular property to the resultant adhesive--thermal stability by the silica, wetting of the adherend metal by the boron oxide, and thermal expansion control by the sodium oxide. Actual application of the dried and ground frit as an adhesive is accomplished as a slip or slurry obtained by milling the frit with water and usually a suspension agent, such as colloidal silica, to a desired consistency, for brush, dip, or spray application to the faying surfaces, and then firing the assembly at specific temperatures, pressures, and times. Although relatively early progress was made in effecting lap-joint bonds of stainless steels of lower ranges of temperature stability, adaptation to the higher range steels and super alloys and refractory metals, and to sandwich construction type bonding has necessitated wide-scale reformulation and reprocessing and a need for new concepts and approaches.

Initial improvements in lap-shear and lap-bend strengths were effected by placing thin metal screens in the bond line, similar to the concept used in reinforcing organic resins with fiberglass cloth. This, however, was not adaptable to sandwich panel constructions because of the difficulty experienced in inserting and maintaining the screen between the coated face sheets and the honeycomb core throughout the firing and maturing cycles. Although additions of fine powder carbonyl iron also made for stronger lap-joints, these additions promoted excessive localized oxidation of the core when applied to sandwich-construction bonding. In like manner, while additions of aluminum oxide promoted increased lap-joint strengths, particularly lap-bend strengths, principally because they imparted greater porosity and therefore greater flexibility to the bond, this porosity was undesirable in attempting to effect a good bond with the thin foil edges, or feet, of the cores in sandwich type constructions.

Probably the most significant of the continuing improvements in the development of ceramic adhesives for metals has been motivated by a concept previously substantiated in the field of porcelain enamels. This is based on the premise that improved adherence between a glass and a metal and improved wetting of the metal surfaces are obtained if the glass contains the oxide of that metal. Relatively easy confirmation of this concept and its possible applicability to ceramic adhesives was obtained with additions of small quantities of ferric oxide to a typical silica-sodium oxide-boron oxide slip which resulted in markedly improved strengths in bonds to steel. Likewise, additions of nickel and cobalt oxides to ceramic-oxide frits have improved strengths of such adhesives when used to bond such nickel and/or cobalt based alloys as Inconel X and Rene' 41. Further strength improvements have been promoted by further applying this principal to the extent of flame spraying a thin film of nickel-chrome alloy to the faying surfaces as part of the surface cleaning treatment prior to adhesive application. Additions of powders of the individual representative adherend alloy metals themselves as well as their oxides, to the ceramic frits and/or slips have also improved bond properties. Powders of the alloyed metals themselves have further contributed. Additions of oxides of metals other than the base metals of a given adherend metal alloy, for instance chromium, appearing in the adherend metal alloy, even though in relatively small percentages, have also contributed to the over-all improvements in strength and thermal stability of the ceramic bonds. Even metals and oxides thereof not even represented in the base adherend metals, for instance zinc and copper, have also contributed in certain measure depending on how incorporated and in what proportions. Eutectic mixtures are not necessarily the best mixtures. The pattern of obtaining an optimum formulation appears to be one of statistical analyses of many candidate materials and possible combinations. The pattern of bonding seems to be approaching that of a brazed joint to the extent of establishing a continuous metal phase. However, increased thermal stability is being realized and the objectionable properties of brittleness and frangibility inherent in glassy bonds are being reduced by these developments. Further progress in these respects is expected from current studies on recrystallized frits, annealed bonds, and bonding mechanism studies.

Feasibility of bonding refractory metal to refractory metal using ceramic bonds has also been demonstrated. These investigations have to a marked degree followed the same approaches used in the work with the lower temperature range metals, - that is, developing a basic glassy frit and introducing the oxide of the particular base refractory adherend metal and other oxides of high melting temperatures. Best bonds whether of tungsten to tungsten, molybdenum to molybdenum, tantalum to tantalum, or columbium to columbium, have been effected where tantalum pentoxide replaced the silica as the primary glass forming agent.

Another current program of work is based on a novel approach involving the use of metal brazing alloy foils in conjunction with vitreous compounds in order to incorporate the favorable characteristics of both materials, the ductility and strength of the braze and the thermal stability of the ceramic. Although the feasibility of this approach has already been substantiated by impressive lap-shear strength data obtained on bonds of various stainless steels, the major objectives of the program are the examination and determination of the mechanism of the interaction between the braze and the ceramic, and in turn the adherend metal, and the examination and determination of the physical and chemical structures of the resultant bonds. Based on initial findings to be determined with stainless steel adherends, it is proposed to further synthesize and formulate ceramic-braze combinations specifically adaptable to bonds of adherend metals of still higher thermal stability such as the nickel or cobalt based super alloys and the refractory metals. X-ray and photomicrograph studies are intended to establish the optimum compatibilities of the candidate materials with radioactive tracer techniques being

employed to establish the mechanism and structure of the bonds. The expected levels of strength for these various approaches to inorganic bonding is shown in figure 8.

Another unique method for joining metals has recently been successfully adapted to the fabrication of metal sandwich constructions.

This method, for which patent applications have been initiated, has been termed the exo-flux method wherein the prefix "exo" refers to an exothermic-reactant composition which, when applied to, and ignited on, the external surfaces of the metals to be joined, imparts an intense instant heat of short, flash duration to a metal oxide "fluxing" agent and element metal donating material which has been placed within the bondline (on the metal faces to be joined) and forms a strong adhesive joint with a continuous metal phase. Under these spontaneous conditions of firing, the metal oxide of the fluxing agent releases its metallic portion to form a eutectic with part of the base adherend metal. Although to date formulations and techniques have been proportioned specifically only for bonds of stainless steels, effective bonds have been made with most of the heat-treatable stainless steels, including 17-7PH, PH15-7 Mo, AM-350, AM-355, A-286, -302, and -321, giving promise that the process may be adaptable also to the bonding of higher temperature resistant alloys such as Inconel X and Rene' 41, and perhaps even the refractory metals (tungsten, tantalum, molybdenum, etc.).

A significant point for the exo-flux method of joining is that it adds relatively negligible weight to a structure so bonded as evidenced by a comparison of the 0.3 lb. per sq. ft. general average of brazing alloy required to effect a brazed sandwich panel and the 0.006 lb. per sq. ft. of exo-flux required to effect the same panel.

Although, as stated, major emphasis is being placed on elevated temperature resistant inorganic type adhesives, two other programs of endeavor in the field of adhesives are worthy of mention even though they are of a "specialized" nature and tied to the lower temperature range organic types. In brief review these are:

1. Room temperature curing adhesives have been in continuing need for field and emergency repair of aircraft where the pressurizing and heating equipment normally required for curing are not available. A two-part, low-pressure, ambient-temperature curing adhesive system based on an amine-cured novolac epoxy resin has been developed which meets prime target strength and pot life requirements. A formulation concept of using metallic chromates as filler materials proved to be a simple yet effective means of overcoming a general susceptibility of epoxy-resin-based adhesives to salt spray and humidity exposures, which susceptibility had also plagued prior endeavors with acrylic and resorcinol type resins.

2. As needs for adhesives of increasingly high temperature resistance have been growing, so also are requirements for adhesives which will resist cryogenic temperatures. This does not imply that both properties must be possessed by any one adhesive--composite construction designs being such that although both conditions of temperature extremes would be encountered within an over-all structure, they will be confined to separated components insulated from each other. Preliminary studies on commercially available organic adhesives of representative chemical types indicate that further development of cryogenic adhesives can be made in the field of organic materials. The preliminary evaluations were limited in scope and, accordingly, other than pointing up a preference for epoxy type adhesives over other chemical types, particularly the vinyls and phenolics, gave no indication of the capabilities of the adhesives under long time exposures, under stressed vs unstressed conditions, in bonds with various different

types of adherend metals, etc. Continuing investigations are designed to establish these and other capabilities and will include formulating to specific end-use requirements if necessary.

Summary

In summary, it is estimated at this time that to satisfy predicted requirements and make available for use the best possible structural plastics and adhesives, research in the following areas must be continued (figure 9):

- a. Matrix materials, both organic and inorganic types, for short and long time use over the temperature range of 500° to 2000°F. Additional specific requirements in this area can be added, such as resins which are particularly suited to filament winding, and inorganic matrix with increased elongation and strength.
- b. New and improved composite reinforcements, including higher strength fibers, higher modulus fibers, and higher temperature resistant fibers, also having low density.
- c. Adhesives with increased temperature capability both for long time use in the temperature range of 500° to 800°F and short times to 2000°F. This includes adhesives suitable for use with super alloys and refractory metals.
- d. Research in the area of fabrication processes, such as filament winding, to achieve maximum obtainable properties with available materials.

BIBLIOGRAPHY

1. WADC Technical Report 58-450, "Survey of Adhesion and Adhesives".
2. WADC TR 58-549, "Heat Resistant Low Pressure Phenolic Resin Glass Fabric Base Laminate".
3. WADC TR 58-555, "Review of Structural Plastics".
4. WADC TR 59-11 and Supl I, "Research and Development on Elevated Temperature Resistant Structural Metal to Metal Adhesive".
5. WADC TR 59-15, "Development of Low Pressure Ambient Temperature Curing Adhesive".
6. WADC TR 59-82, "Research and Development on Inorganic High Temperature Adhesives for Metals and Sandwich Construction".
7. WADC TR 59-113, Parts I, II, and III, "Research and Development on Inorganic High Temperature Adhesives for Metals and Composite Materials".
8. WADC TR 59-328, "Heat Resistant Laminating Resins".
9. WADC TR 59-600, Parts I, II, and III, "Mechanism of Fiber Reinforced Structural Plastics".
10. WADD TR 60-24 and Supl I, "High Modulus, High Temperature Glass Fibers for Reinforced Plastics".
11. WADD TN 60-287, "Properties of High Modulus Reinforced Plastics".
12. WADD TR 60-299, "Synthesis of Fiber Reinforced Inorganic Laminates".
13. WADD TR 60-791, Parts I, II, and III, "High Temperature Resins, Analysis of Process Parameters, and Evaluation Procedures for Filament Wound Composites".

APPARENT DEFORMATION BEHAVIOR OF SPECIMEN IN FLEXURE AT 800 °F

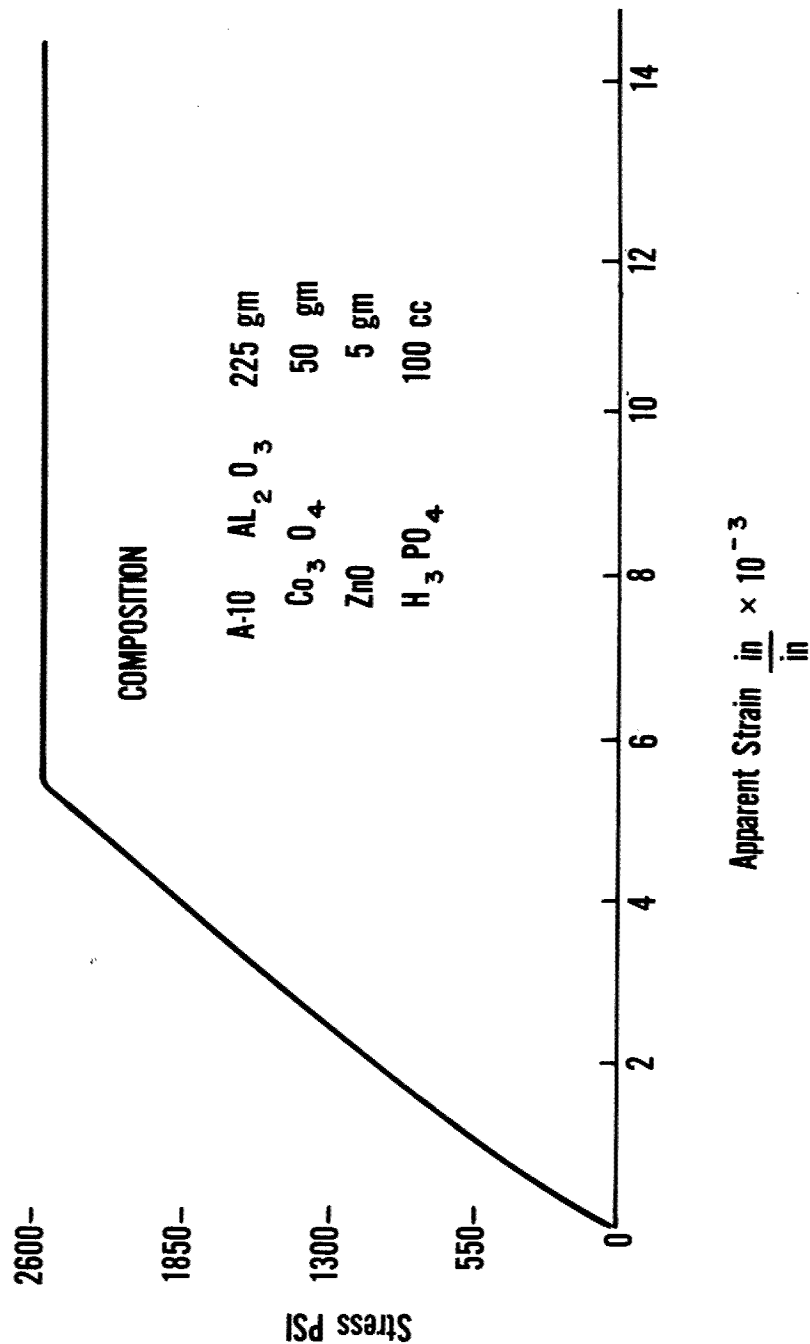


Figure 1. Load-Deformation Curve and Composition of Inorganic Matrix Material

STRENGTH PROPERTIES OF YM31A COMPARED TO 'E' GLASS REINFORCED PLASTICS

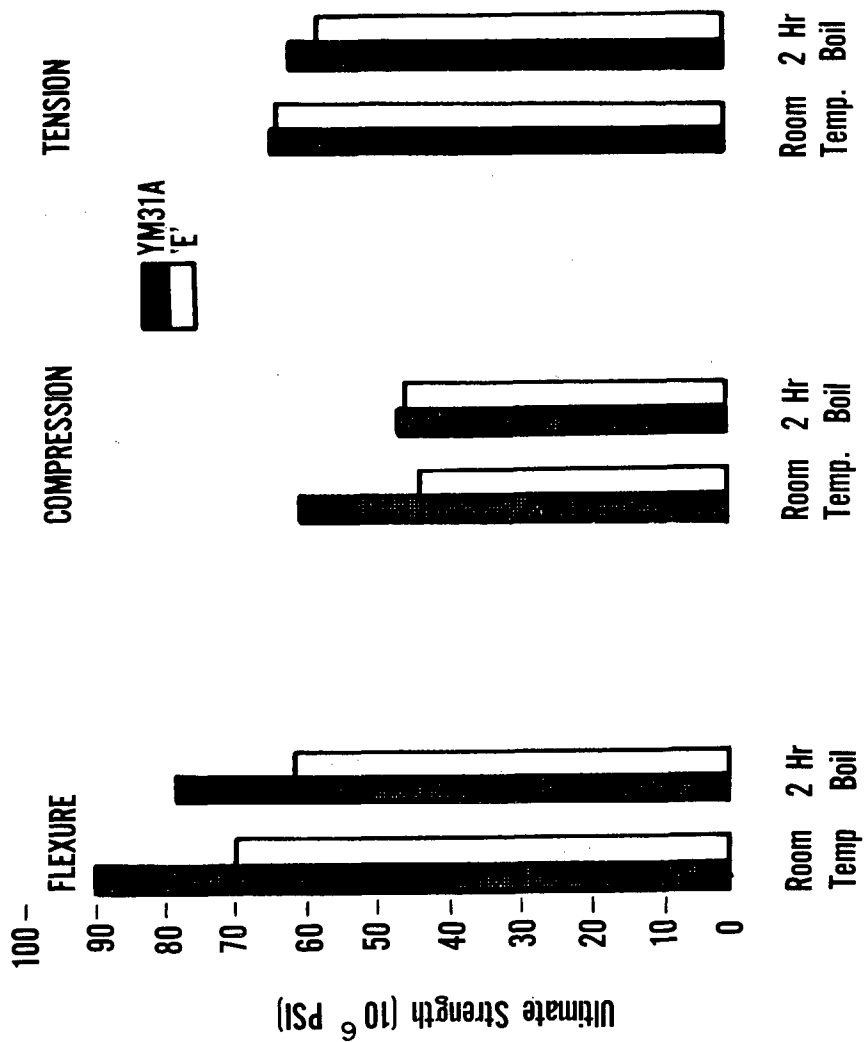


Figure 2. Strength Properties of YM31A Compared to "E" Glass Reinforced Plastics

MODULUS PROPERTIES OF YM31A COMPARED TO 'E' GLASS REINFORCED PLASTICS

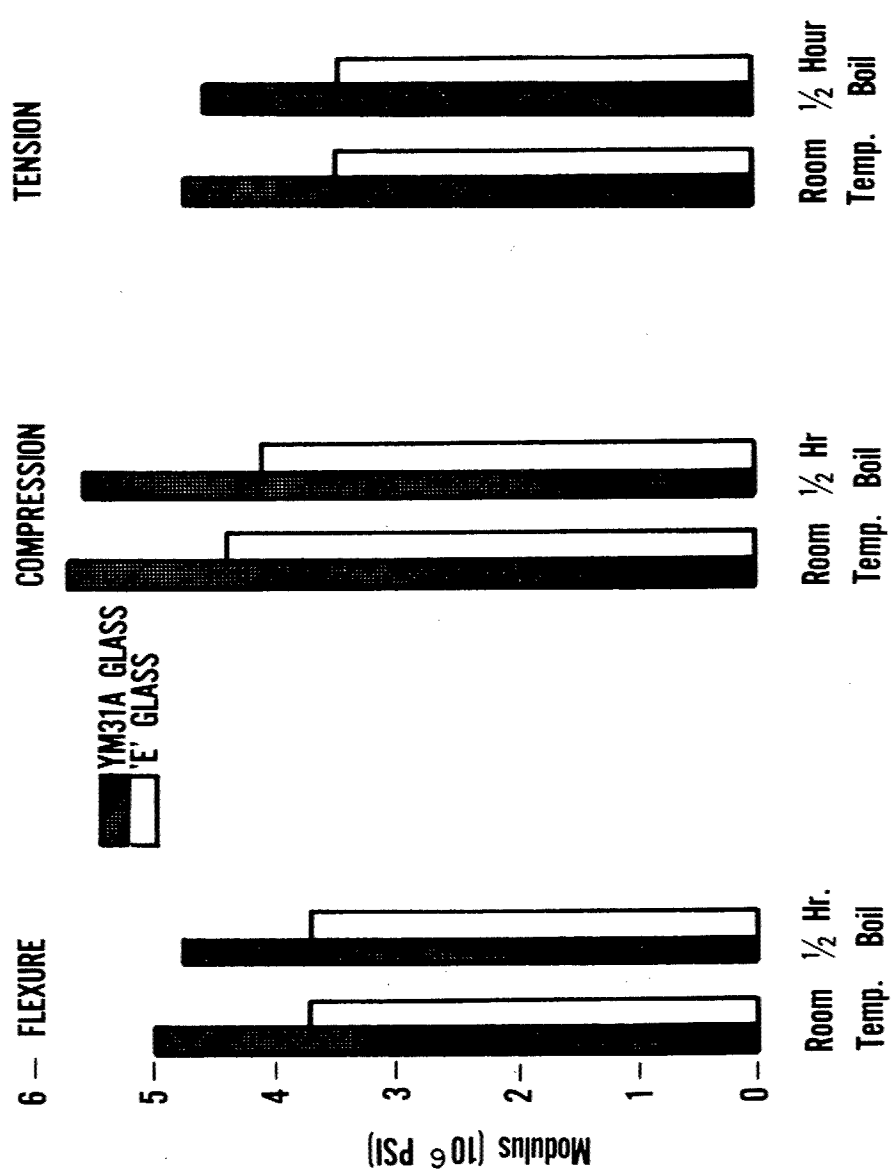


Figure 3. Modulus Properties of YM31A Compared to 'E' Glass Reinforced Plastics

STRENGTH OF GLASS FIBERS AT ELEVATED TEMPERATURES

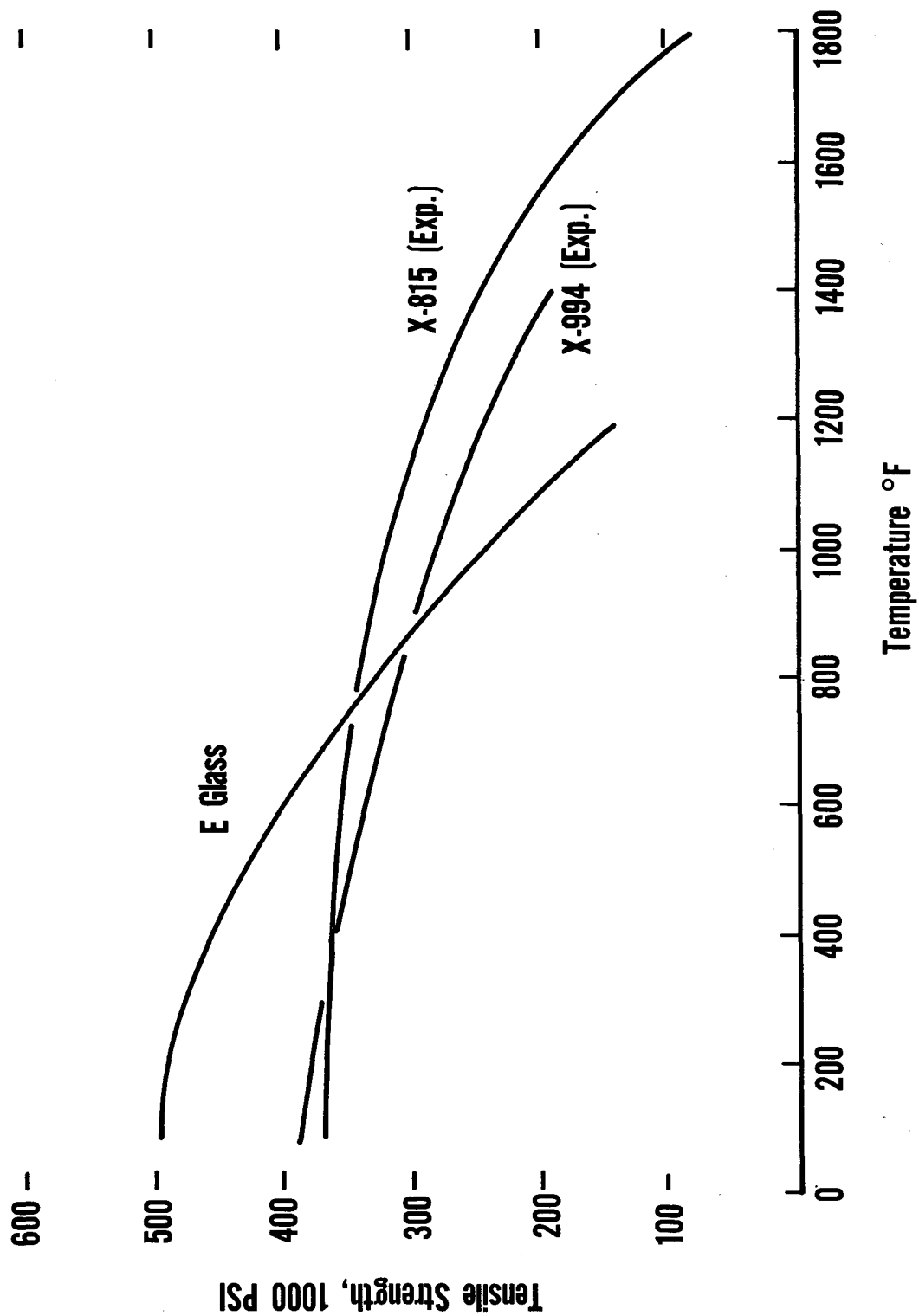


Figure 4. Strength of Glass Fibers at Elevated Temperatures

PROPERTIES OF SOME PRESENTLY AVAILABLE STRUCTURAL MATERIALS

	Glass Fiber—Resin Filament Wound	Steel	Titanium
Density(lb./in ³)	0.075 0.080	0.285	0.163
T.Y.S., psi	250,000 (Unidirectional) 225,000	220,000	150,000
Strength/Density in. x 10 ⁴	193 160	78	92
Modulus of Elasticity, psi x 10 ⁶	5 8.5	30	16

Figure 5. Strength Levels of Currently Available and Experimental Filament Wound Composites

ORGANIC ADHESIVES

SHORT-TIME TEMPERATURE RESISTANT CAPABILITIES AND LIMITATIONS

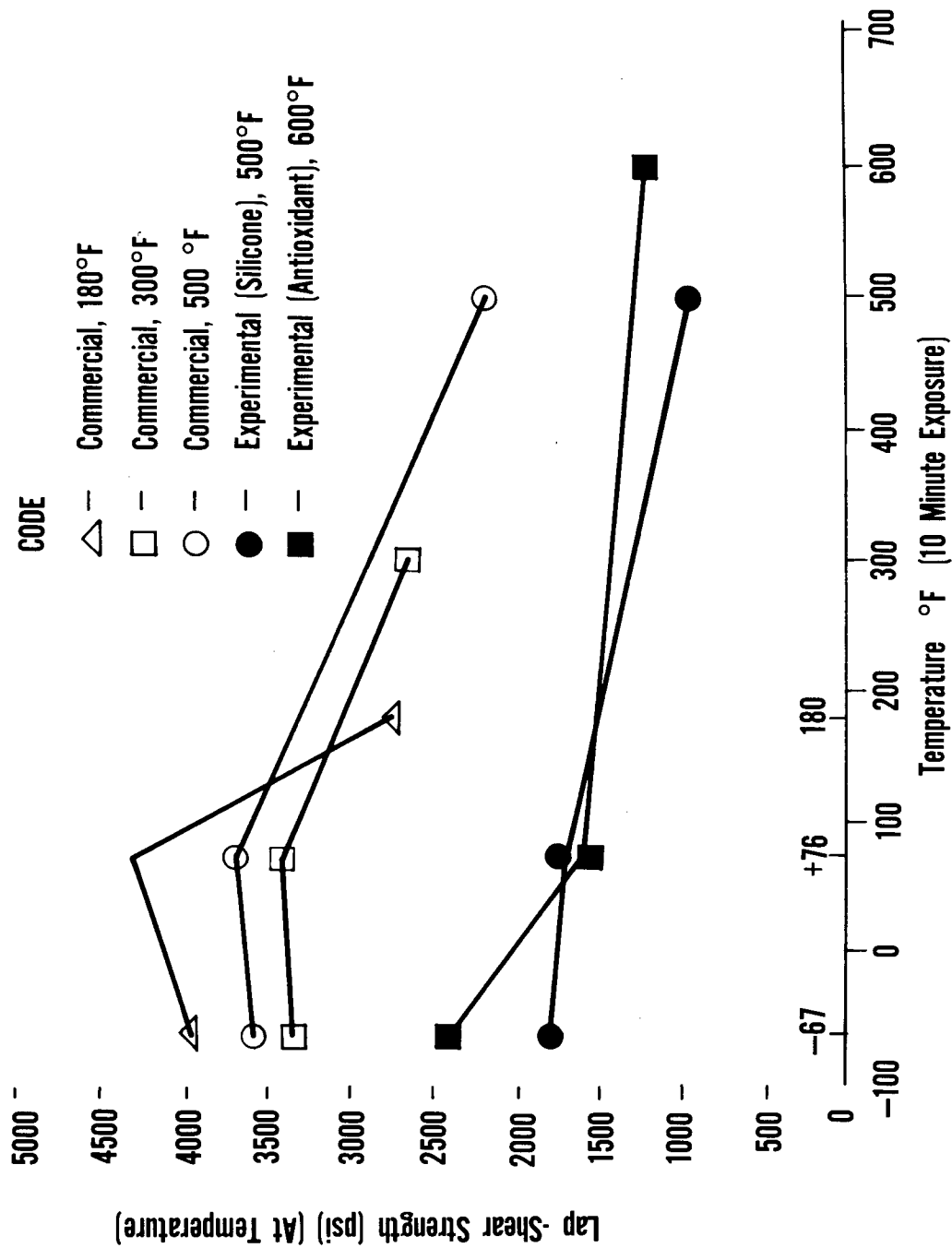


Figure 6. Organic Adhesive Bond Strengths—Short Time at Temperature

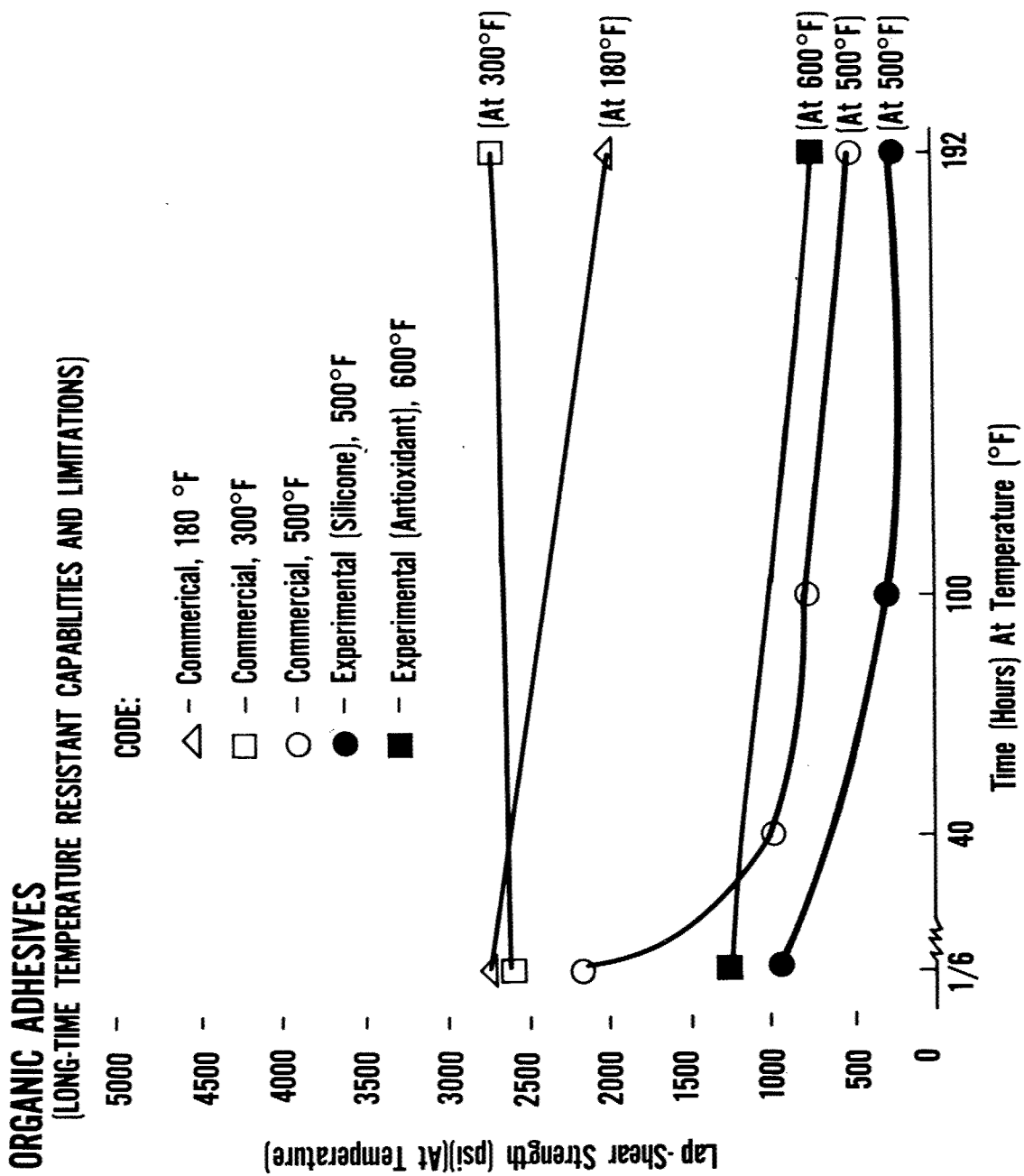


Figure 7. Organic Adhesive Bond Strengths—Long Time at Temperature

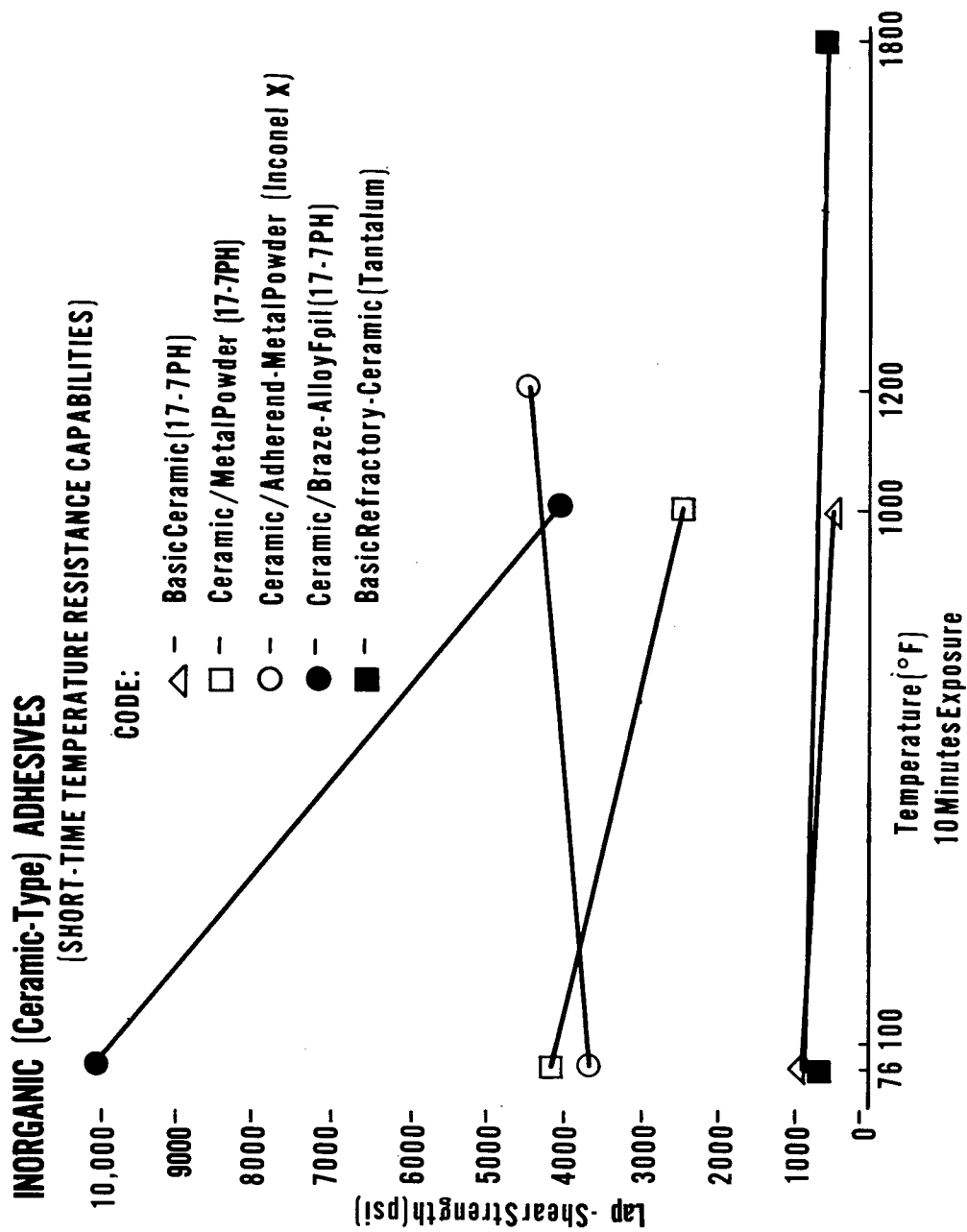


Figure 8. Inorganic Adhesive Bond Strengths—Short Time at Temperature

**DESIRED MATERIALS RESEARCH FOR
IMPROVED NONMETALLIC STRUCTURAL COMPOSITES**

MATRIX MATERIALS

Organic

Inorganic

REINFORCEMENTS

High Strength

High Modulus

High Temperature

ADHESIVES

Improved Temperature Resistance

Improved Strength

FABRICATION PROCESSES

Figure 9. Desired Materials Research for Improved Nonmetallic Structural Composites

PROTECTION OF REFRACTORY METALS AGAINST ATMOSPHERIC ENVIRONMENTS

Chairman

Mr. O.O. Srp

Speaker

Mr. N.M. Geyer

Panel Members

Mr. T.D. Cooper

Lt. L. Hjelm

Mr. J. Meyers

PROTECTION OF REFRACTORY METALS AGAINST ATMOSPHERIC ENVIRONMENTS

N.M. Geyer

Directorate of Materials and Processes, ASD

Introduction

Materials with various special capabilities at very high temperatures is presently one of the main concerns of the materials engineer. The refractory metals, molybdenum, columbium, tantalum, and tungsten, are prime candidates for several applications in hypersonic flight and re-entry vehicles. In such structural uses these metals may be subjected to a variety of total environments such as different temperatures, heat fluxes, dynamic pressures, and mechanical loads. However, one factor of all potential structural environments can be generalized—a refractory metal will be exposed to air at elevated temperatures.

If the so-called "refractory" metals were truly refractory such a condition would not pose a serious problem. Unfortunately the refractory metals' behavior has been more nearly that attributed to chemically reactive metals, i.e., refractory only in a mechanical sense, by retaining relatively high strength at elevated temperatures. At high temperatures, especially temperatures above 2000°F, all four refractory metals suffer from the highly undesirable property of reaction with atmospheric gases. Although, serious variations in mechanical properties can result from reactions of these metals with nitrogen and hydrogen, the extremely rapid, frequently disastrous, reactions of the refractory metals with oxygen represent the most serious problem. Indeed the problem of preventing oxidations of the refractory metals at the very temperatures of their potential use probably represents the greatest remaining deterrent to their utilization as structural materials.

Oxidation

The severity of the problem of oxidation of the refractory metals cannot be overstated. Data accumulated by numerous investigators confirm the extreme rapidity with which each of the four metals reacts with oxygen. Tremendous amounts of information have been generated in efforts to characterize the oxidation of various alloys of the refractory metals, most of which have been experimental alloys formulated in attempts to develop oxidation-resistant compositions. Despite these widespread efforts very little understanding of the true nature of the oxidation reactions which occur has been achieved beyond phenomenological explanations, i.e., the kinetics and mechanisms of oxidation of the refractory metals have not been satisfactorily described. A more complete understanding and consistency in oxidation theories would be helpful in defining the problems so that adequate protection of these metals from deterioration in oxygen atmospheres may be achieved.

Since the actual oxidation of the refractory metals cannot then be discussed in any detail, a brief review of the characteristics of reaction is pertinent to illustrating the depth of the problem.

The oxidation kinetics of any metal are usually expressed mathematically through one of several relationships according to the time dependent nature of the reaction. The relationships most commonly referred to are logarithmic (or inverse logarithmic), cubic,

parabolic, and linear equations wherein either film thickness or weight change is expressed as the corresponding function of time, e.g.:

$$w = k \log t - C \quad (1)$$

$$1/w = A - B \log t \quad (1a)$$

$$w^3 = k_c t \quad (2)$$

$$w^2 = k_p t \quad (3)$$

$$w = k_l t \quad (4)$$

where w represents either film thickness or specific weight change (weight per unit area); k is a rate constant; A , B , and C are constants; and t is time.

The logarithmic relationships describe thin film growth, cubic equation empirically describe growth of some thicker films, and the parabolic relation expresses growth of adherent protective thick films (scale) where reaction rate is probably controlled by ionic diffusion, as proposed by the classical Wagner-Hauffe principle. Linear (also accelerated or a symptotic) oxidation rates occur when reaction products are porous, nonadherent, molten, or volatile; these situations usually pertain to the refractory metals at these temperatures of greatest interest.

The progress of oxidation with time for each of the four metals under review has been frequently investigated, most commonly by measuring weight increases in oxygen or air at various temperatures. The agreement between investigators on the time laws in effect for each metal is as quite consistent, i.e., the shape of the curve of weight gain vs time plots is quite reproducible. Results are summarized cryptographically as follows:

	500°F	900°F	1200°F	1600°F	2000°F	2300°F
Mo	PAR	PAR-LIN	LIN			
W	PAR	PAR-LIN	LIN			
Ta	LOG	PAR	PAR-LIN	LIN	ACCEL	
Cb	LOG	PAR	PAR-LIN	LIN	ACCEL	

where log is the logarithmic reaction rate; par, the parabolic reaction rate; par-lin, parabolic with transition to linear rate; lin, linear reaction rate; and accel, the accelerated or a symptotic reaction rate. Oxidation of the refractory metals can be generally described as being parabolic at low temperatures, progressing to an initially parabolic with transition to linear reaction rate at intermediate temperatures, and subsequently becoming linear at higher temperatures (ranging from 1000°F for Cb and Ta to 2200°F for W). Some quantitative idea of the magnitude of the oxidation reactions of the refractory metals is presented in representative curves for oxidation of the four refractory metals (figures 1 and 2).

Figure 2 shows oxidation rates as a function of temperature over the temperature range from 1000°F to 2000°F. Higher temperature data is quite meager and difficult to correlate. Data has been obtained under such widely variant conditions of time, temperature, atmosphere (air or oxygen), and pressure (both total and oxygen pressures) as to make a plot such as this at best only approximate. These curves represent average data from three different investigators at the indicated temperatures in atmospheric pressure air, with times of 0 to 16 hours for Ta and Cb and 0 to 20 minutes for tungsten used to establish the reported rates. Oxidation of chromium at 2000°F under similar test conditions is shown as a point of reference. Molybdenum could not be shown here since the evaporation of MoO_3 at temperatures above about 1200°F renders such weight gain data useless; the oxidation becomes so rapid that virtually no data exists relative to oxidation rate of pure Mo above 1000°F. Tungsten is similarly difficult to characterize at still higher temperatures (above 2000°F).

Figure 2 compares the oxidation of the four refractory metals at 2000°F in terms of displacement of the metal-air interface at various reaction times. Such a plot serves to illustrate in a practical sense the effect of oxidation in removal of metal from an unprotected substrate. Material losses are potentially disastrous after relatively short times at even a comparatively low temperature, i.e., low compared to contemplated utilization temperatures for refractory metals. For example, we can visualize from this plot that a half-inch molybdenum rod would be completely consumed by oxidation after about six hours at 2000°F. The necessity for providing some means of averting such catastrophic behavior is evident.

Contamination

In the discussion of oxidation behavior of the refractory metals, an additional consideration asserts itself. From the oxidation rate curves shown it would seem reasonable to conclude that oxidation of molybdenum or tungsten, being so rapid as to be best described as catastrophic, poses a more serious problem than that of columbium and tantalum. Such is not the case, however, since this supposition overlooks a critical characteristic of the latter metals. Columbium especially, and to a lesser extent tantalum, exhibit great susceptibility to subsurface embrittlement due to high solubility and diffusion of oxygen. This phenomenon known as contamination occurs inevitably upon exposure of columbium to oxygen, even at fairly low temperature, and constitutes the first step of the gross oxidation reaction. The importance of this behavior lies in its deleterious effect on metal mechanical properties, combined with the fact that depth of contamination and accompanying embrittlement may easily exceed metal loss by surface secession. Upon any significant degree of oxygen contamination (and parts per million may be significant), the base metal is drastically changed in properties—increasing in hardness, losing ductility, and exhibiting higher temperature for ductile-to-brittle transition. Since the affected zone normally may include an amount of metal twice that converted to oxide, it is seen that contamination can render columbium totally useless structurally long before the effect of gross oxidation becomes important, or perhaps even observable. Thus susceptibility of columbium to contamination is a vital consideration in judging potential capability of any coating or alloy scheme for protection.

Protection from Oxidation

On the basis of the foregoing data it is not unreasonable to assert that the applicability of refractory metals to high temperature structural designs will be measured eventually by the ability of materials engineers to solve the problem of oxidation protection. In general there are two possible approaches to the protection of the refractory metals from

oxidation: (1) the metal may be alloyed with one or more other metals to produce a protective oxide film; or (2) a coating may be applied which will provide protection by limiting access of oxygen to the substrate metal. Whichever approach is employed, the protection has to be accomplished without materially altering the desirable properties of the bare metal, i.e., especially high temperature strength and resistance to thermal shock and impact damage.

Alloying

The first general approach to protection of the refractory metals, that of alloying, has received considerable attention, particularly for columbium. There has been a modicum of success in discovery and development of ternary or quaternary compositions which represent considerable improvement in oxidizing behavior over the unalloyed metals, and there are actually columbium alloys extant which are comparable to the superalloys in oxidation resistance at 2000°F. However, the alloying solution cannot be described as having been successful in any case for two important reasons. First, the exhibition of good oxidation properties appears to be mutually exclusive with retention of desirable elevated temperature strength, ductility, and fabricability. Second, and actually most important, at any sufficiently high temperature that the refractory metals are attractive for structural applications on the basis of their physical or mechanical properties, there exist no alloys of adequate oxidation resistance for practical use. Moreover, on the basis of present experience and our limited understanding of the principles of oxidation of alloys, there appears very faint hope of any eventual development of such alloys.

Coating

The inability of alloying to provide a workable solution to the problem has channeled research efforts toward development of suitable coatings. This need actually has been clearly understood for several years now, and coating development by the laboratories of numerous organizations has recently been at an increasing rate. The remainder of the discussion will necessarily deal with the current state of the art of refractory metal protective coatings. The field of applications for such coatings is so broad, we will restrict the survey to those coatings currently under advanced development for use on leading edges or under surfaces of re-entry vehicles.

The overall problem of producing satisfactory protective coatings for the refractory metals and their alloys resolves itself into two principle areas. The first has to do primarily with development of protective coating compositions which will combine with the base metal to form compatible, useful materials systems. The second portion of the problem entails development of optimum techniques for application of coatings which exhibit maximum reliability. These two problem areas, although closely interrelated, will be discussed individually to simplify their treatment.

Coating Systems

The criterion for protective coating compositions is that the coating and base metal should not be considered separate entities but, rather, parts of an integral materials system. This interrelationship becomes much clearer when the requirements to be levied against the coating are studied. The basic primary function of the coating of course is that of a barrier to prevent access between oxygen and the refractory metal substrate. Thus, the coating must deter transport of oxygen or oxygen-containing species to the base metal and, conversely, must prevent movement of metal ions to the coating-air interface. The second major necessity is that the coating remain stably in place

throughout the duration of utility of the substrate. Therefore, the coating must be tightly adherent, and diffusion of coating constituents into the substrate and volatilization of coating must be minimized. The coating and basic metal must be chemically and metallurgically compatible. Fluxing of the coating due to interactions such as eutectic formation between oxidation reaction products of coating and base metal would, as would diffusion of the coating constituents, either deplete the necessary constituents or cause deleterious effects on substrate mechanical properties.

The coating must form a mechanically compatible system with the substrate and should not be deleteriously affected by such conditions as stress imposed by either mechanical or thermal loads. Favorable to this condition is a coefficient of expansion of the coating closely approximating that of the base metal; otherwise, extremely high stresses are produced within the coating and at the coating-metal interface during temperature cycling. Also of great advantage in maintaining physical integrity of the system is the ability of the coating to withstand flexure such as that imposed by vibratory loading and possession to some degree of ductility to permit the coated piece to deform under creep producing loads. A situation to be avoided is the possible introduction of notched effects in the coating which may reduce its physical strength because of the characteristic brittleness accompanying this mechanical design.

In addition to the desired properties of the coating already enumerated, i.e., oxidation resistance, stability, and compatibility, it is highly desirable that the coating be capable of resisting damage from impact—both particle and mechanical—as well as erosion or abrasion. Although severity of these requirements depend somewhat on precise applications, we should be cognizant of the possibility of accidental damage during processing, fabrication, and handling of coated parts.

Still further criteria for measuring potential effectiveness of any prospective coating include general surface condition, coating emissive characteristics, and required thickness of the coating to achieve the desired level of protection. In the case of coated aerodynamic configurations, where air flow characteristics are important, a smooth finish is obviously desired. Coating emittance may be of little importance in most applications, but a re-entry vehicle skin temperature can vary several hundred degrees depending upon the surface emissive characteristics; thus, a high-emittance surface can lead to lower operating temperature and indirectly reduced severity of protective requirements. Since weight is one of the principal concerns of aerospace designs, a most desirable feature of any protective coating is its ability, with only a thin layer, to provide adequate oxidation protection for the metal substrate. In the case of fabricated sheet components, we could anticipate that a thick coating could contribute a major portion of total structure weight.

Selection of a composition to serve as a protective coating is far from simple. Probably no coating could meet all requirements imposed by the "ideal", and therefore any coating developed will probably represent a series of compromises between desired properties and those realizable. The actual degree of success in developing coatings for each of the refractory metals is in some measure dependent on the means by which a coating is applied or formed in place on the substrate.

Coating Techniques

Method, i.e., techniques, sequence of operations, and processing parameters of coating application, exerts considerable influence on the success of protection achieved by the resultant coating. Among the techniques available, at least in principle, for forming

protective layers on refractory metals are cladding, electroplating, electrophoresis, liquid-phase chemical decomposition, flame-spraying, slipcasting (enameling), vacuum metallizing, slurry coating, and vapor deposition (including decomposition, chemical reduction, and pack cementation, and variations thereof). There are advantages and disadvantages associated with each technique, and each adapts itself especially to deposition of certain classes of material. Brief discussions of each technique follow, with more thorough treatment of those methods which have been found best suited to protecting the refractory metals.

Cladding

Historically, cladding has been successfully applied to protection of steel and aluminum. This approach demands the ready availability of an oxidation resistant alloy composition which is both compatible with the substrate and amenable to rolling and subsequent bonding operations. There are currently no such refractory metal alloys available, and the development of any such material would be a very considerable undertaking, if feasible at all. The development of a procedure to apply even a single alloy as a clad is in itself a major project. In addition to the fact that they must be applied only to sheet prior to joining or forming operations, claddings suffer a basic disadvantage in that they generally do not protect edges and cut or machined surfaces. Cladding is an unlikely candidate for protecting the refractory metals, with the somewhat remotely possible exception of platinum group metal claddings in certain highly specialized applications.

Electrodeposition

Electrodeposition from aqueous solution has been widely used to protectively coat steels and other metals from corrosion or low temperature oxidation. A great number of metals are depositable from aqueous solution and additional metals are depositable from fused salt electrolytes. Electroplated nickel and chromium were thoroughly evaluated as coatings for molybdenum several years ago, and proved protective at relatively low temperatures. Although electroplating is a relatively simple and convenient technique, deposits are characteristically porous, are not metallurgically bonded to the substrate, and tend to be brittle and nonadherent when plated on refractory metals which have not had complex pretreatments. Generally, extensive post-plating heat treatments would be required to obtain desirable coating properties. Many metals are depositable from aqueous solutions but unfortunately the very ones of greatest interest to refractory coatings (Si, B, Al, Be, Ti, and Zr) are not so depositable, and fused salt techniques are not sufficiently advanced in most cases to provide suitable means of deposition either. This fact, coupled with difficulty in coating intricate shapes, seems to rule out electroplating for application of most coatings; again the principal exception appears to be deposition of platinum group metals as intermediate layers or special coatings.

Electrophoretic Deposition

Electrophoretic deposition is primarily a technique for depositing oxide or metal powders, requiring subsequent densification (usually by isostatic pressing) and sintering. A valuable technique for forming certain composites not readily deposited by other means, electrophoresis is, in its present state, a quite cumbersome technique and has not been used in any large scale refractory coating development.

Chemical Deposition

Deposition from liquids by chemical catalytic decomposition has been achieved for certain metals, primarily nickel, gold, and certain platinum group metals. It is an extremely simple process by practical measure, involving complex chemical reactions. None of the more interesting metals for refractory coatings have been reported deposited by this technique, and it is not likely that it can be used except as a substitute for electroplating.

Slip Casting

Slip casting is of greatest interest in its familiar role of deporting oxides from powders suspended in volatile media which are subsequently driven off before or during "firing" or bonding heat treatment. Resultant coatings are frequently porous and have not shown great promise in protecting refractory metals. Sound metallurgical bonds are frequently difficult to achieve, but in any event simple oxide coatings have satisfactorily permitted ready transport of oxygen to the base metal. Despite disadvantages, this method remains in consideration for those applications where it is desirable directly to deposit an oxide coating, since no other approach to that task is adequately advanced. An offshoot of this approach, termed slurry coating, will be discussed in greater detail.

The technique of hot dipping wherein the part to be coated is immersed in molten metal and the desired coating formed by reaction usually followed by diffusion heat-treatment is well known and widely practiced for depositing zinc, tin, aluminum, and other metals. Where the process is applicable, it is straight-forward and economical. It is possible to deposit metals of higher melting points by dissolution in low melting diluents such as lead or tin, or as alloys with aluminum. However, difficulty is encountered in coating large or complex shapes uniformly, due largely to temperature differences created by varying material thicknesses and clogging of inaccessible areas. The principal value of hot dipping presently is to serve as a simple small-scale technique for applying experimental compositions for laboratory evaluation.

Vacuum Deposition

Vacuum deposition, frequently referred to as vacuum metallizing and sometimes confused with vapor deposition, is a technique capable of depositing virtually any metal, as well as certain other materials. However, until now, vacuum deposition has been limited to formation of thin films; maximum thickness of coherent coatings obtainable by the technique has been considerably less than one thousandth of an inch. Thus, the technique currently has little potential for depositing oxidation protective coatings for refractory metals, since after brief exposure to temperature no coating remains unreacted with either substrate or environment. Another disadvantage is the limitation to line-of-sight deposition.

Of considerable interest because of its ability to deposit quite refractory compositions of an almost unlimited variety of materials is the arc-flame spraying technique, an off-spring of flame metallizing. Both forms of the technique, oxyacetylene and arc-flame spraying, possess the advantage of requiring no heating of the substrate above a few hundred degrees, as well as that of having the capability of rapid deposit of many thick layers. Major problems encountered in flame spraying are porosity of deposits, frequently poor adherence, and difficulty in applying thin deposits; and, post heat-treatments are often required to densify and bond coatings. Conventional flame spraying is normally conducted under oxidizing conditions and therefore the coating is applied

unsintered. Arc-spraying (most often and somewhat erroneously referred to as "plasma" flame spraying) however, can be accomplished in inert or reducing atmospheres; in addition, it possesses wider applicability due to higher operating flame temperatures. The versatility of this technique has given rise to a new concept of coatings, the so-called gradated metal-oxides; the composition of the coating overlay is varied continuously from 100-percent metal at the substrate-coating interface to 100-percent oxide at the surface by varying the material fed into the flame. It is, of course, possible similarly to gradate combinations of metals' oxides or intermetallics and combinations thereof. Despite the promise of this approach to solve certain problems, several barriers remain to its widespread utilization: density and porosity are difficult to control; coatings of uniform thickness or suitable thinness, especially to edges and complex configurations, are difficult to apply; and coating interior surfaces may indeed be frequently impossible.

Vapor Deposition

The area of vapor deposition, often confused with vacuum deposition through loose terminology, is receiving proportionately the largest share of attention in development of new coating systems for reasons which will become apparent. There are three major subdivisions of vapor technique, thermal decomposition, chemical reduction, and pack coating. Each of the first two is variously referred to as vapor plating, vapor deposition or gas plating, and the third is commonly known as either pack cementation or pack diffusion. By whatever title, the latter is by far the most widely adopted technique at present for application of coatings, especially silicide-base coatings, to the refractory metals. A recent survey performed by a subpanel of the MAB indicates that approximately 60 percent of all current coating development efforts utilize the pack cementation technique. Most familiar examples of this technique are siliconizing and chromizing of steels, and recently of molybdenum. The process consists generally of immersing the metal to be coated in a mixture of powders containing the metal element(s) to be deposited, carrier compounds (usually halides), atmosphere controlling compounds (such as ammonium compounds), and inert filler material (usually alumina); the whole pack is charged in a sealed retort and heated for several hours, in the absence of air, at temperatures between 1600° and 2200°F. The essence of a pack process depends then on both thermal decomposition and displacement reactions of metal halides; the reaction temperatures lead to diffusion to form the required coating compounds and to produce metallurgical bonding. Since more than one halide can be present in the retort at any one time, quite complex coatings can be formed. The principal disadvantages of the pack method are: the requirement for long term heating of substrate at high temperature, which sometimes results in recrystallization; the requirement for uniformly heating very large packs and maintaining them at temperature for long periods, and occasional problems of removing sintered powders from coated surfaces, especially internal ones. The corresponding advantages of the process are considerable. It simultaneously forms and bonds the coating in place, a virtually unlimited number of elements can be deposited, operation is relatively simple and readily adjusted by proper selection of reactants, and the process is readily adapted to complex part geometry. Pack coating certainly deserves much of the enthusiasm which it is presently being accorded; however, pack cementation may not be a panacea to the coating problem since better solutions may present themselves for specific requirements.

Other variations of vapor deposition have not received such widespread attention. Both the chemical reduction and thermal decomposition approaches usually employ a flowing gas stream, which contains appropriate vapor reactants, and is passed over the substrate to be coated. Reactions are similar to pack reactions, except that reactants must be continuously added internally. Several metals can be deposited by thermal decomposition of

halides on very hot surfaces; however, necessity for attaining and maintaining extremely high base metal temperatures (over 2200°F) imposes severe limitations especially for specimens of practical size. The alternate method of hydrogen reduction of volatile metal halides, at lower temperatures (1200-1600°F), has received deservedly more attention. This technique yields dense adherent coatings of most metals and can be adapted to deposition of refractory compounds, i.e., silicides, carbides, and perhaps oxides. Although it is not as versatile as pack coating, but rather, more cumbersome and somewhat limited by directional characteristics of deposition from streaming vapor, vapor deposition will continue to be of interest in applying protective refractory coatings.

As mentioned above, thermal decomposition of halides imposes temperature limitations too great to be considered practical. However, a similar process of current interest involves thermal decomposition at low temperatures (about 500°F) of organo-metallic compounds. Certain metal alkyls, carboryls and cyclic compounds have been successfully used in depositing nickel, chromium, and aluminum; and various similar materials could be considered for applying refractory coatings. This process is usually referred to as gas plating to differentiate it from other modes of vapor phase deposition.

Slurry

One other coating technique, which is based on long known practices, but has only recently been adopted to coating refractory alloys, is slurry coating. Here, powdered reactant materials (metals and activators) are suspended in an appropriate vehicle (usually organic) together with possible binders, thickeners, and suspension agents to form a slurry. The slurry is applied cold to the work piece by painting, dipping, or spraying; a bake treatment at low temperature is applied to volatilize the vehicle; and a diffusion heat treatment is performed at 1800° to 2100°F for a few hours in inert atmosphere or vacuum. The resultant diffusion coatings are quite similar to those formed by vapor processing and possess the advantage of simple application and less severe thermal treatments. Uniform thicknesses are attainable on different surfaces because of liquid flow into relatively inaccessible areas. This technique, widely used in depositing ceramic layers, is fairly new as applied to metal deposition and appears to offer very great promise in developing refractory metal coatings.

Overall Requirements

In all the foregoing discussions regarding coating application methods there has been a strong implication of necessity for convenience and simplicity of technique as well as necessity for uncomplicated specimen geometry. Despite the fact that the prime concern before the laboratory investigator is to discern a coating capable of protecting some refractory metal, the ultimate consideration is to protect adequately fabricated structures in a practical, user situation. Let us pause to consider what this includes: most importantly, how well and how long the protection is afforded, without failure. (This should not be an "average" figure.) This is the factor which governs the necessity for extensive evaluation and testing of myriad coated specimens and the establishment of failure criteria. Other aspects of practicality involve time and temperature requirements and the economics of coating processing. One further consideration is repair or reprocessing of imperfect or damaged coatings. A truly versatile coating process for which conditions were such that mishaps in processing did not predicate discard of valuable parts, and that local damage or premature failures could be repaired without adverse effects on properties of previously coated regions. These may be vital considerations as they apply to complex shapes such as re-entry vehicle designs utilizing refractory sheet. Additionally, assembly of structural sections could be accomplished by welding or riveting, which would further require that edges of all holes or joints be adequately coated.

Current Development

Overall current status of coating development for the refractory metals can best be described as that of advanced laboratory development, ranging in intensity from very extensive effort for molybdenum and its alloys, through substantial effort for columbium, to almost negligible effort for tantalum and tungsten. Transition from laboratory development to experimental full-scale coatings is well underway for certain molybdenum coatings and planned for coatings for columbium. A survey of current efforts shows nearly fifty organizations (including industrial, governmental, and institutional) actively engaged in research, development, or evaluation of refractory metal coatings. Among these, over thirty are concerned with coatings for molybdenum, about twenty (many the same) are working with columbium, and only about ten are actively concerned with either tantalum or tungsten. Of these totals it is estimated that about thirty organizations are actively pursuing development efforts; the remainder are mostly concerned with property evaluations. A large number of these efforts are under direct government sponsorship or a result of other government programs. A total of about sixty "coatings"—the term coating here designating a particular application technique utilized to deposit a prescribed composition—have been reported in all, with the considerable majority (about forty) properly designated as primarily intended for molybdenum.

Further analysis of current effort shows over half of all efforts are devoted to development of pack cementation processes, and a similar proportion of total effort concentrated on coatings dependent on silicides for their protective features. Almost all coatings being developed, regardless of substrate, are (with the exception of ceramics) composed of some alloy or intermetallic combination of four principle elements: silicon, chromium, aluminum, or titanium, with certain other occasional additions such as boron and carbon. Virtually every known empirical approach was employed in pioneering efforts toward protecting molybdenum, and subsequent work on the other three metals has tended to follow the same trends established there. Thus, an almost disproportionate degree of effort has been and continues to dwell on optimization, scale-up, and establishment of reliability for those coatings found most successful to date for protecting molybdenum under such conditions as will be encountered in re-entry vehicle leading edge applications. This work is well-founded and designed to fill urgent immediate needs, but an unfortunate side effect has been dilution of remaining available resources for research and laboratory development of new coating concepts applicable to differing requirements of other base metals and applications. This remaining effort is nevertheless being applied profitably to development of new coatings and adaptation of application processes.

Status of current programs to protect each of the refractory metals is summarized briefly in the following remarks. Most of the coating developments outlined below have been with specific reference to unalloyed substrates of each metal under discussion. In the case of the Group VI metals, i.e., molybdenum and tungsten, it does not appear critical to distinguish between various alloys as possible substrates requiring coating. It is not likely that the low level additions to which structural alloys of Mo or W are limited would exercise sufficient variation in total chemical characteristics to significantly alter protective ability of a particular coating composition. On the other hand, when considering Group V basis metal substrates, tantalum and columbium, it is quite important to distinguish between abilities of various coatings to protect different alloys, since alloys based on Cb and Ta frequently contain large percentages of different classes of additives, and the chemical behavior of alloys in relation to the ability of a coating to provide protection is subject to considerable variation. For example, a coating which displays great potential for protecting high-titanium alloys of columbium may be less promising or even entirely unimpressive in its ability to protect tungsten-bearing alloys. Throughout the

ensuing discussion, therefore, it is essential to remember the possible substrate variations when considering potential utility of different coatings for each refractory metal.

Molybdenum

As noted previously, primary effort for molybdenum is concentrated on pack-silicide coatings. This is the result of a tremendous amount of evaluation which has indicated the advantage of this type of coating over others promulgated over the past several years. To discuss in any detail the findings of the numerous evaluations which have been performed would be an undertaking both tedious and so large as to be completely beyond the scope of this discussion. A minimal background discussion, however, will show why this approach has evidenced itself as the prime candidate for reliably protecting molybdenum under specialized re-entry conditions.

Widespread past development efforts have employed almost every application technique to form a wide variety of protective compositions on molybdenum. Earliest efforts to coat protectively molybdenum were aimed at protecting heater elements. Historically, emphasis then shifted to protection of turbojet engine components; during this phase most of a wide variety of coatings were initially developed. As, more recently, interest centered on ramjet parts and now on aerodynamic structural applications, the requirements imposed, evaluation required, and testing performed have likewise undergone changes in emphasis so that now a vast array of data can be assayed to show a number of interesting coatings produced for molybdenum, depending on the intended use. Included among coating systems explored for molybdenum have been the following:

1. Electroplated coatings of nickel, chromium, various precious metals, and especially chrome-nickel composites;
2. Flame sprayed nickel-chrom-boron and nickel-silicon-boron, aluminum-chromium silicon, molybdenum disilicide, and refractory oxides;
3. Vapor or pack-deposited siliconized and/or chromized coatings; clads of platinum and nickel alloys;
4. Enameled coats utilizing chromium or zirconia frits; and
5. Hot-dipped (or solutionized) coatings of chromium and aluminum-silicon.

For purposes of comparison, generalized average data pertaining to exhibited properties of some of these various coatings is summarized in table 1, which is extracted from a DMIC report on molybdenum coatings. Such a compilation can only serve to provide general comparisons and more recent data may be available in many cases. The coatings represented in table 1 have been widely tested under varying conditions; all data must therefore be viewed with a highly critical attitude. However, such information does permit a broad view of relative capabilities of the various coatings of part or current interest for molybdenum.

Briefly extracting the data reflected in the table, the ensuing remarks serve to summarize molybdenum coatings. The pack diffusion silicide-base coatings-- of which at least four commercial variations currently merit consideration-- provide the longest protected lifetimes at all temperatures above 2000°F. Although reliability has not been sufficiently demonstrated to satisfy exacting requirements imposed by aerospace designers, it appears higher than for most other coating types. Resistance to thermal

shock at high temperatures is good and hot ductility is reasonably satisfactory. Primary problems lie in low temperature brittleness of the coatings and attendant mechanical effects on the coated substrate. The most interesting coatings from among others previously developed for molybdenum were: (1) the nickel-chromium electroplated alloys, which possessed excellent oxidation resistance and fair reliability at intermediate temperatures; and (2) the flame-sprayed nickel-silicon-boron, nickel-chromium-boron and aluminum-chromium-silicon compositions which provided excellent oxidation protection and reliability, fair thermal shock characteristics, good hot ductility, with no detrimental substrate effects, but suffered from the typical foilings resulting from the inaccessibility of sprayed coatings to complex surfaces, and poor coverage of vulnerable corners and edges. Although it has since been surpassed in favor by the pack-coatings for aerospace vehicle application, the various nickel-chromium compositions still offer a degree of feasibility for certain special applications.

Columbium

Progressing to columbium coatings we find substantially less total effort and no clear-cut standout success among candidate coating systems. At least three approaches to protecting columbium appear quite promising and merit discussion. At first, development efforts toward columbium coatings followed the same general course as molybdenum coating research had undergone earlier. One expected consequence of that fact has been the establishment of pack-siliconizing as one method of adequately protecting columbium. However, performance of the silicide base coatings on columbium has not been nearly as spectacularly superior to other coating systems as it has been for coating molybdenum. Lifetimes achieved with this coating system are not so long at similar temperatures, and processing conditions apparently tend to more seriously affect properties of the base metal. In general, comments regarding these coatings on Mo can be similarly stated for Cb in greater or lesser degree.

In contemplating protection of columbium, an additional problem arises; not only must columbium be prevented from reacting directly with oxygen to avert structural loss of material, but the attendant oxygen contamination of the base metal with severe effects on substrate mechanical properties must be solved. Still another potential problem is the elimination of hydrogen from those processing steps where that gas might react readily with the Cb to produce unfavorable changes in substrate properties. For these reasons at least two additional coating systems, which have demonstrated potential protection from oxidation and contamination, bear further serious consideration for protecting columbium.

The first such promising coating to be discussed is the vacuum-pack deposited Cr-Ti-Si alloy. In this approach, columbium is packed in metal powders of 50 percent chromium and 50 percent titanium, and heated in vacuum to produce deposition of the Cr-Ti alloys and simultaneous diffusion; subsequently, a layer of silicon is similarly produced. The resulting ternary composition is capable of protecting columbium and alloy substrates for periods reproducibly exceeding ten to twenty hours at 2400°F. The principal advantage of the process is that the coating overlay and diffusion zone are essentially metallic in nature, and exhibit considerably more ductility, both hot and cold, than coatings based on intermetallics. Small quantity additions of halides to the vacuum-pack result in much more rapid deposition at lower temperatures, and also result in longer term, more reliable protection. The coating, which completely eliminates detrimental hydrogen and oxygen from the processing scheme, is not only protective against external oxidation reaction, but also eliminates contamination effects in the same temperature regime. One obvious problem arises in further utilizing this combined pack-vacuum vapor process; the necessity for maintaining high vacuum, although an important advantage in the

processing environment, represents a major requirement possibly in conflict with practicality of coating application on a commercial scale. Further efforts on effects of additives to the pack might substantially alleviate this difficulty, however. From the standpoint of protection afforded, this vacuum-pack process has shown best results on columbium; the problem of adopting the process to potentially large-scale applicability remains to be completely solved.

The third coating scheme of major interest in relation to columbium, besides pack-silicides and vapor-pack chromium-titanium alloys, consists of slurry-depositing aluminum alloys, which form complex columbium aluminides on diffusion heat treatment. As an application technique, the slurry method possesses a major advantage in simplicity, including relatively low temperature and short processing periods. Also, the slurry aluminide coatings appear capable of providing adequate protection for columbium at temperatures up to 2500°F. Such a coating—an aluminum-silicon-chromium alloy applied by dipping or spraying—has successfully protected a large complex structure for a required time of 2 to 10 hours at 2500°F; thus, practical feasibility has been demonstrated. This coating system, perhaps, does not possess as great maximum protective capabilities as the other two but it exhibited practicality which may be more critical in the long run for the particular applications under consideration here.

Along with the approaches discussed in detail above, a considerable amount of coating development effort has been expended for columbium, resulting in a number of interesting systems. The current status of these programs is illustrated in table 2, which is extracted from a contract state of the art survey conducted for the Air Force by Thompson Ramo Wooldridge, Inc. Among systems which have received more than passing interest have been the zinc dip coating developed by Naval Research Laboratories, a series of hot dip aluminum alloys and sprayed alumina sealed with refractory glasses. The zinc dip coating has displayed an amazing capacity for correcting coating flaws and has demonstrated good protectiveness, but at temperatures far below our range of present discussion (1800° to 2000°F). The glass impregnated alumina coating, commonly designated "system 40," has demonstrated reliable protection of columbium for periods up to 500 hours at 2300°F. However, the coating is quite thick and heavy and suffers all the disadvantages in practicality ascribed to flame sprayed coatings. The various hot dip aluminizing treatments have lead to the development of the slurry coating process previously discussed, and appear to offer little advantage to compensate for difficulties of application to large or complex shapes. Data for other columbium coating systems is shown in the table and is self-explanatory.

The columbium coatings effort revolves about the requirement for optimization and selection from among at least three concepts currently considered most promising. Any of the three is probably capable of supplying the required protection, thus selection is wholly dependent upon the particular application considered. Further information on relative properties of the various coatings, as compared on identical samples of base metal and tested under exactly similar environments, will be available in Part II of ASD Technical Report 61-66, and should be of value in discerning advantages and limitations of each approach. Present indications are that each of the coatings discussed will have reached a status comparable or superior to that of present molybdenum pack cementation coatings within the year.

Tantalum

Until one year ago the status of protective coatings for tantalum could be described adequately in one word—nonexistent. Since then, however, interest in tantalum has been

heightened because of the properties exhibited by several experimental alloys. Aside from a few experiments where some tantalum specimens were added to the "batch" while processing molybdenum or columbium coatings, no information of real value had been produced on tantalum coatings until the new interest in tantalum alloys prompted the Air Force to sponsor two exploratory efforts. These new programs, based largely on previous work with columbium, have shown feasibility of protecting tantalum and its alloys for periods of varying length at temperatures to 3000°F and beyond. One effort has dealt primarily with the now familiar pack siliciding process and has indicated feasibility on a small laboratory scale of protecting tantalum alloys by that approach. Protection periods of 6 to 10 hours at temperatures up to 2800°F have been reproducibly recorded with either chromium or aluminum-modified silicide coatings. A second major effort has dealt with formation of aluminide coatings, first by hot dipping, and subsequently, after interesting compositions had been noted, by slurry coating. A number of compositions provided promise; however, an unusual coating has provoked greatest interest. As part of the hot dip studies, tin was utilized as a diluent to permit greater control of dipping time and temperature. The coatings produced by this means retained residual tin phases and such coatings performed extraordinarily well, providing complete protection reliably for 10 to 20 hours up to 2900°F. Subsequent study has shown that similar tin-bearing aluminides produced by slurry dipping, painting or spraying give still better protection, with lifetimes of 100 hours up to 2800°F and for a few hours above 3000°F. Apparently this unique coating depends upon a thin film of alumina for protection and the aluminum-bearing tin sublayer provides a reservoir of aluminum to heal flaws in the film. The coating is very simple to apply, appears quite reproducible, and withstands a surprising degree of physical abuse in addition to providing oxidation and contamination resistance. Also interesting is that the same coating provides good protection to molybdenum substrates (for somewhat shorter periods than for tantalum). One other approach to protection of tantalum has been cursorily studied: the formation of tantalum beryllides on the metal surfaces by vapor phase reaction with beryllium. Such coatings appear intrinsically quite oxidation resistant, but have not borne up well under thermal shock and react by diffusion quite rapidly with the base metal. (The latter effect is considerably reduced on tungsten containing alloys.) The beryllide approach still seems worthy of further investigation; however, silicides are presently more promising, and aluminides (especially the tin-aluminum system) appear best suited to long term high temperature protection of tantalum.

Tungsten

Tungsten, the one refractory metal not discussed thus far, remains an enigma so far as protective coatings are concerned. Results of only a very few preliminary feasibility efforts are available for comment. Electroplated rhodium, over complex alternate layers of silicon and chromium, has successfully protected resistance heated tungsten wire for about one hour at 3000°F. Vitreous bonded zirconia has protected tungsten wires at temperatures up to a reported 3600°F for about three hours. Siliconized tungsten wires have survived exposure to flowing 3300°F air for as long as ten hours. All these results have been quite tentative and have not been very reproducible; poor reliability is indicated by available data. There have been reports of similar protection by plated platinum or iridium, but all these approaches are limited by melting point considerations. We do not anticipate serious consideration of tungsten for structural applications until we encounter environmental temperatures exceeding 3000°F. Apparently other studies are being conducted on a proprietary basis. Some reports of flame spraying and pack coating have been circulated, but not substantiated. In comparison with the other refractory metals, little effort is being expended on developing protective coatings for tungsten. It is clear that tungsten will require protection at all temperatures above about 1300°F; it is equally

clear little effort is currently being devoted to clarification and development of possible solutions to this problem.

From meager available information it appears probable that stable oxides will be the necessary protective species on which any coating for tungsten is to be based. On this assumption, one effort has been newly initiated to study the problem of forming thin metal-bonded oxides on the surface of tungsten by controlled reaction of deposited inter-metallic coatings at reduced oxygen pressures. Another program, Air Force sponsored, is seeking to definitely establish those parameters and material properties, a knowledge of which is necessary to logical formulation of a coating development program. At the extremely high temperatures contemplated for utilization of tungsten, thermo-dynamic and kinetic considerations will demand a thorough understanding if any hope of providing practical solutions to the protection problem is to be realized. We highly recommend that resources of industry, as well as those of government agencies, be enlisted in accomplishing the many tasks which form portions of the overall problem of providing some protective scheme to enable use of tungsten in atmospheric environments approaching 3500°F.

SUMMARY

The state of development of coatings for protection of the four refractory metals in atmospheric environments can be summarized briefly as follows: Pack cementation coatings are available which appear capable of providing required protection for molybdenum; new applications continue to impose further demands, however, which may not be readily met; therefore, continuing efforts to optimize present coatings are required, and room remains for new approaches. Altho no single coating for columbium is so fully advanced as the pack-silicide coatings for molybdenum, at least three, the vacuum vapor Cr-Ti-Si alloy, the slurry aluminide, and the pack silicide types, appear quite promising for providing necessary protection. Coatings for tantalum are comparatively new and unexplored; both silicide and aluminide coatings show great potential, and tin-bearing aluminide coating developed for tantalum looks especially promising, both for tantalum and the other refractory metals. No coatings for tungsten have progressed beyond laboratory feasibility studies or very early development. The total picture thus presented consists of a balance between severe problems and promising developments.

A number of special problem areas have been either mentioned briefly or implied. Obviously the first requirement of any protective coating is that it survive exposure at the environmental conditions, i.e., at any particular temperature. Probably the second major problem area is that of practicality of coating systems. A logical extension of this problem is the potential repairability of coatings; the ultimate in practicality would be a coating system amenable to spot repair (or patching) of either damaged or imperfectly coated specimens. Another prime requirement is the standardization of coating evaluation procedures. If any progress is to be made in the always difficult area of standardization of test techniques, it will be necessary to recognize that responsibility for testing against specific design requirements has to be delegated to design and applications engineers, while laboratory testing procedures should be standardized to give completely comparable data for various systems from which selections for advanced testing can be made. To guide the thinking and planning of coatings producers, more complete requirements in terms of total environment need to be spelled out by prospective users of coated refractory metal alloys. Accompanying this need for dovetailing of requirements information and coating development plans is a requirement for both realistic simulated service test development and nondestructive inspection procedures. Also, proper and/or possible sequences of operation and compatibility of various joining and coating procedures

deserve separate study. Closely associated with this problem is the ever increasing pressure on the part of aerospace designers to utilize thinner and thinner gage sheet metal parts. Very little can be said regarding that problem, except that the popular and presently most reliable diffusion-formed coatings may be greatly reduced in applicability under such conditions.

There exists a continuous need for related efforts in support of coating development. Since direct effort developments are made on a basis of meeting immediate requirements, it is quite probable that resulting coatings suffer disadvantages necessitating design compromises. For example, diffusion may well represent mode of failure of many coatings; thus development of diffusion barrier layers may well be required. Also, the long term necessity for development of ceramic-base coatings for temperatures above 3000°F on tungsten and tantalum points the way to study of novel means of forming such compositions on metal. These related development efforts should include both investigations of feasibility of various application techniques to form classes of coating compositions and also development of alternate techniques to form specific proven compositions. The problems of developing added features of ductility and "self healing" should also be attended. Related efforts then revolve about the study of new application techniques and novel coating compositions. Despite gratifying progress recently in coating refractory metals, the need for original and unique approaches to solution of the problem continues.

A review of knowledge regarding oxidation protection of the refractory metals discloses, in addition to the above general problems, several areas of fundamental research where information is needed to support development efforts: mechanism of oxidation both of the refractory metals themselves and potential coating materials; nature and chemistry of oxidation products; and deterioration of coatings by physical processes, i.e., diffusion and volatilization. This is a fairly wide spectrum of fundamental investigation which is required to provide basic information for more intelligent coating development effort as opposed to strictly empirical "hit-or-miss" coat and test programs.

CONCLUSION

The oxidation of unprotected refractory metals is so rapid as to be properly termed disastrous. Of the two approaches open to adoption for solution of this vital problem, alloying to form oxidation resistant composition has been extensively tried and found wanting. The remaining alternative, development of protective coatings, has been recently explored quite extensively. As a result of these efforts, coatings to reliably protect molybdenum appear attainable for certain special applications. At least three interesting coatings are being developed for columbium. Several avenues appear promising for protecting tantalum. And, preliminary efforts indicate feasibility of protectively coating tungsten at lower than anticipated use temperatures. Many problems stand before the realization of development of practical reliable coatings for these metals, and recommendations in the areas of process optimization, supporting development, and fundamental research have been provided.

COMPARATIVE OXIDATION RATES

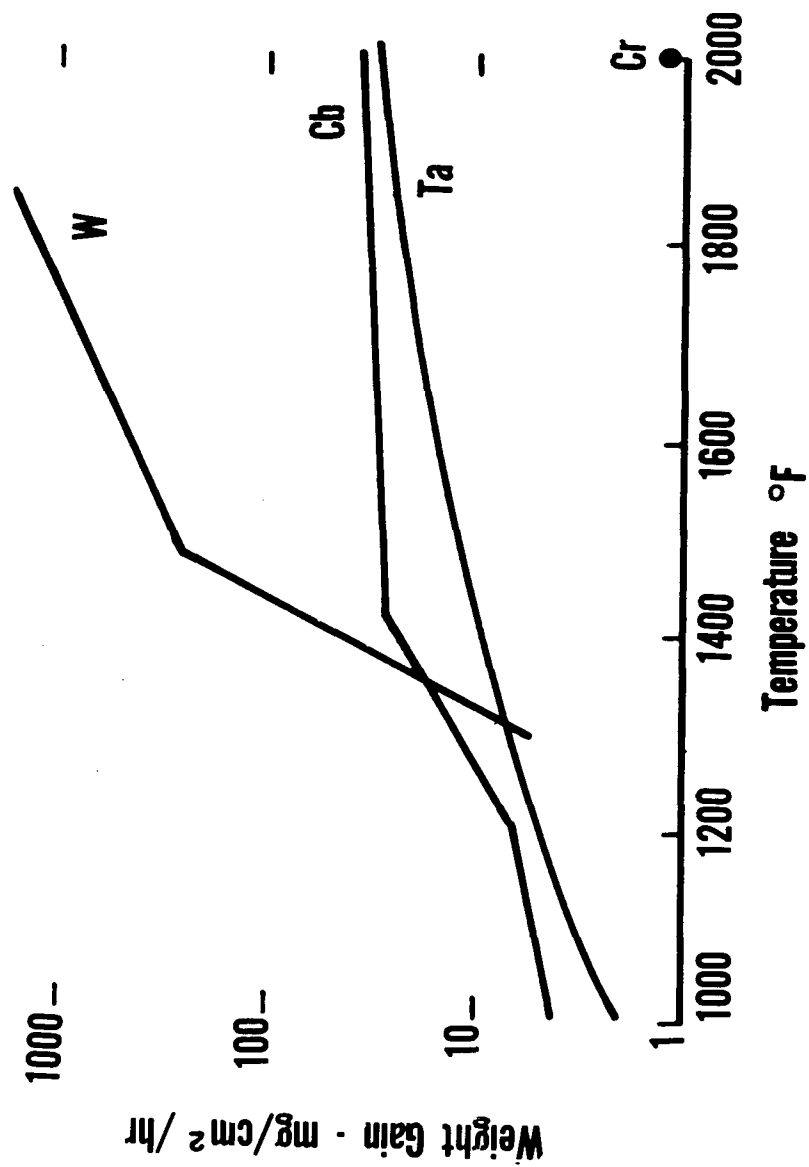


Figure 1.

SURFACE RECESSION AT 2000°F

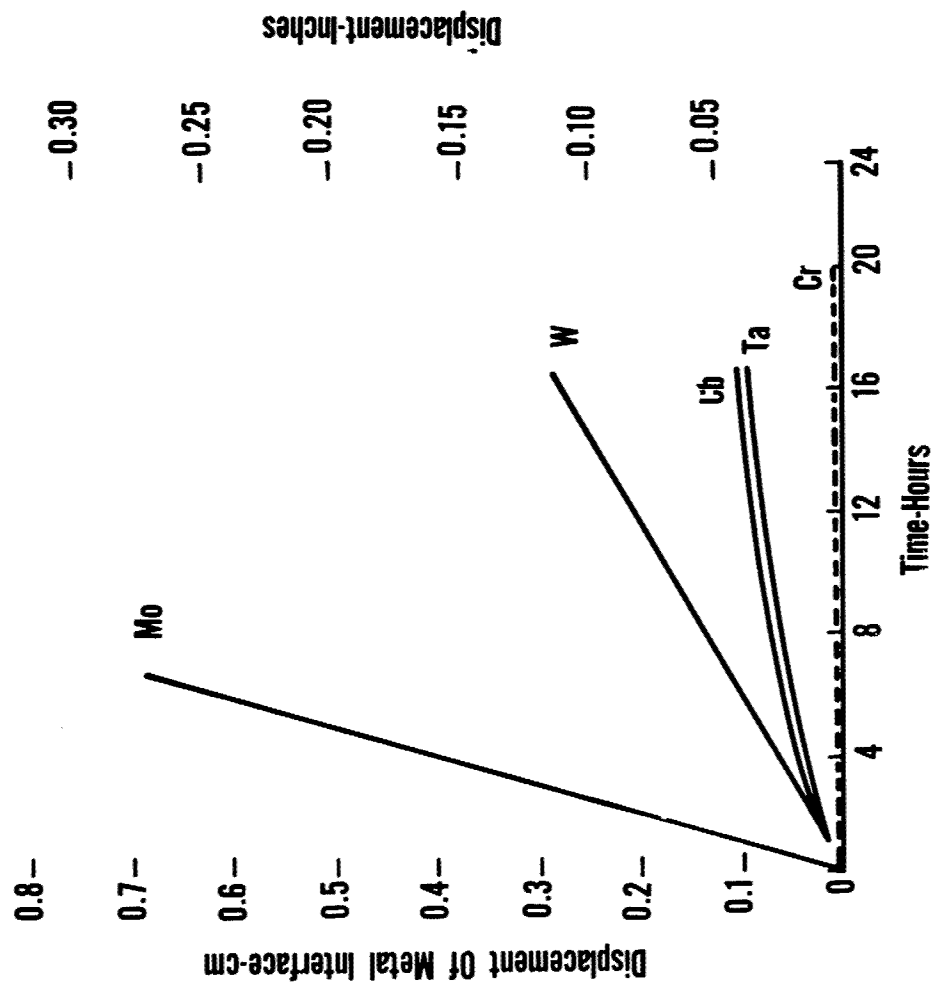


Figure 2.

ENERGY TRANSPORT AND THERMODYNAMIC BEHAVIOR

Chairman

Mr. L. Salsberg

Speakers and

Mr. P.W. Dimiduk

Panel Members

Dr. E. Rutner

Mr. A.K. Hopkins

VAPOR PRESSURE MEASUREMENT

Paul W. Dimiduk

Directorate of Materials and Processes, ASD

The usefulness of thermodynamics as a tool in materials engineering has been discussed in many standard texts on thermodynamics over the last century. More recently its utility both for predicting materials performance in various environments, as well as for materials synthesis, has been rather thoroughly treated by many outstanding figures such as Brewer, Margrave, and others. Its use however, has been severely restricted at the temperatures of current interest because of a lack of the fundamental data needed to carry out the calculations. These considerations in addition to those of elucidating the processes involved in vaporization constitute the main impetus to the measurement of vapor pressures.

Vapor pressure is that pressure exerted by a vapor when it coexists in equilibrium with its condensed phase. This simple statement is not at all indicative of the difficulties the modern experimenter encounters in examining systems of interest. To begin with he must find an inert vessel to contain his sample. At high temperatures he is bound to have a head-on encounter with what appears to be the first law of High Temperature Chemistry: namely that "At high temperatures all substances react with each other, with the measuring instruments, and on many occasions with forms of matter which the experimenter would swear were not even present in the room." A quick check of this law can be made by anyone attempting to measure any property of any material at temperatures of 2000°K or above. This in essence is the "container problem" which rules out the classical static and transpiration methods so familiar to many workers in other fields of chemistry

The second major problem centers around the fact that if a pressure can be measured by means of one of these methods, it represents a total pressure which in turn is made up of the sum of the individual partial pressures of the various species present in the vapor. The species in the vapor may bear little resemblance to what might be expected from a knowledge of the composition of the condensed phase. It is evident then that measuring vapor pressures at high temperatures is centered around that of construction of equipment made of suitable materials and the determination of vapor species. The most widely used techniques are based on the kinetic theory of gases, and are commonly referred to as the "Knudsen" effusion method and the "Langmuir" method.

The Knudsen Effusion Method

The Knudsen method is based on the consideration of molecular effusion of an ideal gas into a vacuum through a small orifice, from a vessel at a given pressure. With this in mind consider a closed, inert vessel of low vapor pressure which contains one or more condensed phases at constant temperature. If the contents of the vessel are in a state of equilibrium, the number of molecules leaving the surface of the condensed material are equal to the number of molecules condensing. Furthermore, the vapor pressure built up within the vessel is due to the number of gas molecules striking any unit surface area within the vessel. Now if the vessel is pierced with a hole whose dimensions are small compared to the mean free path, the molecules striking the area of the hole will effuse and can be counted and characterized. The effusion under such conditions will not affect the equilibrium in the vessel or change the pressure. With these conditions in mind, the

relation derived from kinetic theory between the rate of effusion and the pressure in the cell is given by:

$$\frac{dn}{dt} = P (2 \pi MRT)^{-\frac{1}{2}} \quad (1)$$

where:

- $\frac{dn}{dt}$ = rate of collision of molecules/cm² of any wall surface = rate of effusion (mole/sec/cm²)
- P = pressure in cell (dynes/cm²)
- M = molecular weight of vapor molecules (g/mole)
- R = gas constant (ergs/deg. mole)
- T = absolute temperature (°K)

With some algebraic manipulation the equation can be written in a form more usable for the experimental determination of vapor pressures:

$$P = \frac{w}{a} \left(\frac{2 RT}{M} \right)^{\frac{1}{2}} \quad (2)$$

where:

- w = rate of effusion = rate of mass loss (grams/sec)
- a = area of effusion hole = net vaporization area (cm²),

and the other symbols are the same as in equation 1.

This is the basic relation used in the Knudsen method, and it can readily be seen that the theoretical basis for it is quite sound. When the experiment can be conducted within reasonable temperatures, on a simple condensed phase which is in equilibrium with a known monomolecular vapor, a simple measurement of weight loss as a function of time can yield quite good results for the vapor pressure at a given temperature.

In practical application, especially at high temperatures, numerous compromises are frequently made whose effects may be known and corrected. But in some cases unaccountable errors may be introduced. The source of some of these errors will be illustrated in the discussion of the specific analysis techniques which are commonly used. The well known container problem which is crucial in high temperature applications will not be discussed, but the next measurement technique will show how it can be completely avoided.

The Langmuir Technique

In the Langmuir method, no container is used and the evaporation is carried out from the unconfined surface of the sample.

The treatment of this situation begins with the fact that the number of molecules leaving the surface of any enclosed, condensed phase at equilibrium equals the number recondensing. If it is assumed that every molecule which strikes this surface sticks, then the

number condensing per unit area is the same $\frac{dn}{dt}$ previously presented by equation 1. And at equilibrium this $\frac{dn}{dt}$ must also equal the rate of evaporation.

In practice there is the possibility that not all of the molecules which strike the surface will find favorable sites for retention by the surface. For this reason a condensation coefficient α is defined as the ratio of the number of molecules condensing on a surface to the total number which strike it. Equation 1 must then be modified to read:

$$\frac{dn}{dt} = \alpha P (2 \pi MRT)^{-\frac{1}{2}}, \text{ (rate of condensation)} \quad (3)$$

all the symbols have been defined above. At equilibrium this expression must also describe the rate of evaporation. This basic equation is then utilized in the Langmuir method by modifying it to yield a vapor pressure at temperature from a measured weight loss rate. The modified version is:

$$P = \frac{w}{a \alpha} \left[\frac{2 \pi RT}{M} \right]^{\frac{1}{2}} \quad \text{(equilibrium evaporation rate assumed)} \quad (4)$$

All the symbols have been previously defined but it must be noted that since there is no orifice, α is now the total sample surface area and not an orifice area.

There are however some disturbing inconsistencies about the coefficient α . It is difficult to see what a condensation coefficient described and defined in the above manner could possibly have to do with evaporation under the conditions of the typical Langmuir experiment on refractory materials. Here there are great pains taken to keep ambient pressures low enough to insure that a particle which leaves the surface will condense elsewhere and never return to the evaporating surface. The α deduced for equations 3 and 4 is clearly α condensation assumed equal to α vaporization. Yet the literature is full of confusing and misleading definitions of α . It has commonly been called a condensation (or sticking) coefficient, and evaporation (or vaporization) coefficient, and an accommodation coefficient. These quantities can all be validly defined but they all differ from each other. All of these names for α appear, frequently with the implication that this is the quantity one would use for the α in equations 3 and 4. Perhaps it would help to use α_c , α_v , and α_a for the respective quantities. The α in equations 3 and 4 is probably most nearly related to α_v . In practice an additional definition has been used and should probably be adopted as α_L :

$$\alpha_L = \frac{\text{vapor pressure determined by Langmuir technique}}{\text{true equilibrium vapor pressure}}$$

It is rather obvious that α_v and α_L especially are ill defined because they are correction factors used to accommodate rates of various surface phenomena to the kinetically determined collision number, α_c . The α 's usually discussed in the literature pertaining to vapor pressure work are actually either α_L or some ratio of α_c and α_v . These α 's could vary widely with experimental conditions. Still another α (perhaps α_c) is of interest where the vapor is being condensed on cold plates during an experiment. The α_a mentioned above relates gross energy transfer per collision with a wall.

It will become obvious that many experiments being conducted often really lie somewhere between the Knudsen and the Langmuir methods. This is especially true of much work claiming to use the Knudsen technique. If the various α 's involved are equal to 1, then useful information can be obtained. If one or more of the pertinent α 's are not at least close to one, the data is certainly going to be ambiguous. The variation of the α 's with temperature and pressure is not understood. Because of these "coefficient" problems and other problems inherent to these techniques it is not surprising that absolute vapor pressure data from various experimenters can vary over an order of magnitude. Fortunately the slopes of the vapor pressure vs $1/T$ curves are more reproducible among various experimenters and therefore the derived heats of vaporization are reasonably reproducible in spite of the great spread in the absolute pressure data. In this same vein a properly conducted Langmuir experiment can be relied upon to yield reliable rates of vaporization for materials heated in a vacuum. This in itself is a valuable piece of design data which does not require an understanding of the vaporization mechanisms.

Methods for Vapor Analysis

As has already been mentioned above that the simplest method for obtaining the rate of vaporization, and consequently the vapor pressure, is a measurement of the rate of weight loss during a reasonable time period at temperature. By this method a measurement at a single temperature could take many hours, in the case of some refractories of interest, and little if any information is obtained on the nature of the vapor. If the vapor composition is not that which is assumed, then only some unknown multiple of the true vapor pressure can be calculated. The weight loss method can be used with either the Knudsen or the Langmuir techniques. Normally the former is considered first with materials of relatively high vapor pressures and where an appropriate container can be found. Where the rates of weight loss are low at workable temperatures, or the container problem exists, the Langmuir method may be considered, to avoid the container problem and to utilize the higher rates of vaporization attendant with the higher temperatures and larger vaporizing surface areas available in this case. The α_L must of course be known or estimable for a valid experiment.

To improve the sensitivity of either technique, the oldest device used is a collimator hole which forms a molecular beam from a calculable fraction of the total vapor effusing from the sample. This beam is then condensed on a collector plate for subsequent analysis. The formula used with a Knudsen cell and collimator has been derived from the kinetic theory of gases with the assumption that the molecules leaving any surface have a cosine distribution and are in the molecular flow regime:

$$f = \frac{D^2}{D^2 + 4L^2} \quad (5)$$

where f is the fraction of the molecules leaving a small (point) ideal orifice, located in a plane parallel to a collimator and on a line joining the centers of the two holes, which pass through the collimator hole for collection or detection. D is the collimator diameter and L is the distance between the orifice and the collimator. The amount of material condensed on the plate is then determined by some method of quantitative analysis such as direct weighing, chemical or instrumental analysis, or possibly by the highly sensitive methods made available by radioactive isotopes and activation analysis. The vapor pressure is calculated from the number of moles of vapor that have been collected through the collimator by multiplying equation 2 by $1/f$. The α_c for simple vapors on the cold metal

plate is assumed to be 1. Notice that species information is obtainable in the methods described so far.

The collimated beam may also be analyzed by other methods to yield both qualitative and quantitative information on the vapor species composition, partial pressure, and rate of vaporization. The most widely used methods for more direct identification are momentum and velocity detection, and both absorption and mass spectroscopy. If separate experiments are set up, emission, absorption, mass, radio frequency, and microwave spectroscopy can yield much direct information on vapor species. Electron diffraction is becoming an extremely powerful tool for elucidating gas phase molecular structure at high temperature. The field emission microscope has been proposed for vapor studies but since gas sorption is involved, little direct information on equilibrium gas phase molecules can be expected.

Devices which may be termed momentum detectors are among the oldest means for directly obtaining a vapor pressure and/or, indirectly, an average molecular weight. If a Knudsen cell, with the orifice in the top, is suspended from a balance; then at any given temperature the force on the balance is the sum of the weight of the crucible plus contents, plus the change of momentum due to the effusing beam. The weight of the tared crucible and contents can be obtained at any time by quenching the furnace temperature. By using equation 1 the rate of mass loss yields only the product $P(M)^{-\frac{1}{2}}$. Combining this with the beam momentum, obtained by difference, will yield an average molecular weight.

A method closely resembling the above is the torsion effusion experiment in which the sample is contained in a cylindrical or box shaped container and suspended in a furnace by means of a fine wire. Two eccentric holes are drilled into the container on the extremities by a diagonal line perpendicular to the support wire. The vapor effusing through the holes exerts a twisting moment on the cell and support wire, causing it to rotate through an angle against the torsional force of the wire. By measuring the angular deflection, the area of the holes and their respective moment arms, and knowing the torsional constant of the wire, the momentum carried by the beam can be obtained. The cell can also be hung from a balance to obtain continuous mass loss data.

The advantages of the momentum detectors are that relatively high background pressures can be tolerated, vapor composition need not be known to obtain a total vapor pressure, an average molecular weight can be obtained if mass loss rate data is also measured, and total pressure data can be obtained rapidly without periodic removal of the sample for weighing. Disadvantages include inability to obtain detailed information on complex vapor species, induction heating techniques cannot be employed unless steps are taken to prevent the magnetic force fields from giving erroneous weights or deflections, and extraneous oscillations are usually present. Another method yielding beam momentum involves measuring the deflection imparted to a loaded plate of known area upon which the vapor beam impinges. This method has the same advantages of momentum detectors but can circumvent some of the disadvantages including the last two mentioned.

The collimated beam can be passed through a mechanically rotated velocity selector to yield an intensity distribution as a function of selector velocity. This intensity distribution is a function of the velocity which in turn is a function of the gas molecular weight. For complex vapors at high temperatures the resolving power is usually poor and the results usually ambiguous.

Methods utilizing magnetic and electrical field interactions with the vapor particles have severe limitations and appear to have little advantage over mass spectroscopy; therefore, no further discussion will be given.

Emission and absorption spectroscopy have little application in the analysis of beams as such, but are valuable where separate experiments can be set up. Absorption spectroscopy appears to have some promise for vapor beam analysis if used in conjunction with the matrix isolation technique. An apparatus of this kind, built by General Electric will be discussed later.

One of the best techniques for obtaining both detailed species composition information together with partial pressure data is the mass spectrometer. Recently two excellent discussions on this kind of study have been given by Porter and Inghram. Inghram's recent treatment gives an excellent discussion of the limitations and techniques involved in the mass spectrometric study of vaporizing samples. A controversy has developed as to whether the Bendix time of flight mass spectrometer or the Nuclide Analysis Associates instrument is the more suitable for vapor pressure determinations. The Nuclide Analysis Associates model is based on a design developed by Inghram utilizing large radius magnetic deflection to separate the ions. The operating principles are basically the same as those magnetic types used in many laboratories over the years. Much improved resolution has been achieved primarily through the use of a 12-inch radius magnetic field instead of the usual 6-inch radius.

The time of flight instrument utilizes a pulsed ionization source in conjunction with properly pulsed extraction and accelerating grids together with a less familiar ion separation principle. The ionized species are all accelerated down a field-free drift tube with the same energy, and arrive at a detector in a time that is proportional to their (molecular weights)^{1/2}. This process is repeated every 100 micro-seconds and gas phase processes which are changing rapidly with time can be detected. The resolution is such that adjacent peaks at about mass 200 are just separated. Usable mass range is in the thousands of atomic mass units with less resolution. Sensitivity is in the parts/million range. The electronics of the time of flight instrument have proven to be somewhat unstable and a source of continuous calibration has been needed to obtain quantitative data. There are some who believe that, if properly used, the time of flight spectrometer can be employed to perform any of the measurements done by Inghram with comparable accuracy.

At this writing no one has been able to obtain experimental results from this instrument to compare in utility with those obtained by Inghram with his equipment. For example Inghram has reported appearance potential measurements down to 1 to 2 ev; the best that has been done with a modified time of flight is ~5 ev. The time of flight has not been used to identify an unknown compound by studying the isotopic distribution of its constituent atoms. Inghram reports that his instrument has sufficient resolution for this work.

It appears safe to say that the Bendix is certainly adequate for the study of the simpler vapor systems where there are perhaps a few relatively stable species with reasonably different molecular weights below 200 a.m.u. Partial pressure of 10^{-8} atm appear to be detectable.

The main advantage of the time of flight appears to be in the fact that the basic machine costs about $\frac{1}{3}$ that of the commercially available version of the Inghram machine and takes up much less space. Further, the time of flight's rapid analysis capability (10,000 individual spectra/sec. and $\frac{1}{4}$ micro second sampling time) allows its use for the study of

the kinetics of rapid gas reactions. The Inghram machine does not lend itself as well to this type of study where concentrations of many species must be followed simultaneously.

It appears that no mass spectrometer utilizing electron impact ionization is capable of directly detecting molecular species with very low dissociation energies. Except for some of Inghram's work, there have been almost no studies done with ionization electron energies below about 5 eV with his type of machine. Dr. White, at Ohio State University, has recently made the time of flight machine perform with this electron energy during his studies on some of the rare earth oxides. But even 1-2 eV appears to be enough energy to fragmentize some molecules and it appears that one must use some other ionization method or abandon mass spectrometry entirely for this type of molecule. Matrix isolation and electron diffraction appear to be good bets in this area.

In summary, it can be said that vapor pressures can be obtained only within a factor of 3 to 5 or more due to the problems associated with the detection and analysis techniques mentioned above. Derived heats of vaporization can be obtained with greater accuracy since the slopes of $\ln P$ vs $1/T$ are generally more reproducible than the absolute vapor pressures. Some of the serious problems and limitations responsible for this lack of reproducibility have been mentioned and it is apparent that a great amount of thought, care, and fortitude are required in these measurements.

In addition to the above, there appears to be many questions that remain to be answered in the fundamental assumptions underlying the Knudsen and Langmuir techniques themselves. Evidence is piling up against universal applicability of basic assumptions that are usually made in these types of studies. The question of α briefly discussed above is only one of these. The classically derived "Clausing" or transmission factors have been shown to have fundamental errors in their derivations. Indeed many questions concerning the validity of the cosine law itself have appeared. In the use of the Knudsen technique, a standard means of obtaining information on the vaporization coefficient is to repeat the experiment with successively smaller orifices and extrapolate the data to zero orifice conditions. In some cases this technique has yielded a pseudo-equilibrium value for vapor pressure which differs from the known equilibrium vapor pressure by orders of magnitude and yet is quite reproducible.

Work must be done on the techniques themselves before an understanding of many anomalies, including those mentioned above, will be gained. Some idea of the severe departures from the ideal conditions previously described will be indicated in the following discussions of contractor equipment.

Description of Some Current Equipment

The following description of equipment being used by Air Force contractors illustrates the kind of compromises usually made in practice. In the ensuing discussion figures describing apparatus being used by the AVCO Corporation and the General Electric Company will be discussed and departures from the ideal experimental conditions should be apparent.

Figure 1 shows the details of two Knudsen cells being used extensively by the AVCO Corp. The cell shown in figure 1a is used where a smaller orifice size than is afforded by that in figure 1b is needed or desirable. It should be noted that the circular orifice of either cell is rather large but still within the Knudsen condition of being smaller in diameter than the mean free path of the vapor molecules. Since the very low vapor pressures of highly refractory materials are being measured the large orifice size represents a compromise made in order to be able to obtain a measurable rate of effusion. The cell is

constructed in two halves to facilitate fabrication of these difficult to machine refractory materials. The possible consequences of this expedient is the fact that an alternate source of effusing molecules must be dealt with. This is, however, minimized by keeping close tolerances, by the use of liners, and the presence of water cooled baffles and collimators which condense out most of the vapor that originates anywhere else in the heated area except from the cell orifice. It should be noted that these cells are more in the nature of cylindrical channels rather than true Knudsen cells. That is, it is not really possible to even approach an equilibrium pressure if the equilibrium pressure is such that it will be significantly greater than the ambient pressure outside of the cell. The two cell halves are heated independently to avoid temperature gradients. As a result only processes which can be considered as having a vaporization coefficient of unity can be studied and a Clausing correction factor is appropriate here. In practice the factor would only amount to a 2 to 3 percent correction in the vapor pressures and is therefore ignored. A Clausing correction for the sloping portion of the channel does not exist though work on this problem is in progress at several universities. It can be seen that the conditions produced by vaporizing from these cells lie somewhere between non-ideal Knudsen conditions and the Langmuir experiment.

Figure 2 is a schematic diagram of the "Simple Effusion Apparatus" utilized by the AVCO Corp. in one phase of their studies. One of the previously described effusion cells is heated by electron bombardment. Temperature gradients are minimized by heating the upper and lower halves separately and by surrounding the whole assembly with a radiation shield. The temperature is measured by sighting on a black-body hole, drilled into the bottom of the cell, with a calibrated optical pyrometer. Using this arrangement it is possible to hold the cell temperature to within $\pm 5^\circ\text{C}$. The water cooled baffles condense most of the vapor molecules which leave the cell orifice at low angles as well as vapors which may originate at other points within the radiation shields such as the support members, electron source filaments, cell surface, or the joint between the cell halves. The targets or condensation plates for the vapor are stored within a cavity built into a liquid nitrogen cooled cold finger for efficient condensation of the vapor. The target and collimator are arranged so that only the vapor in approximately a 5-degree solid angle strikes the collector plate. The entire apparatus is pumped to pressures sufficiently low so that the target surface is within a mean free path of the cell orifice; therefore, once a molecule leaves the orifice it cannot reach the target if it has undergone a collision with another gas molecule or a surface other than the target. The cold finger aids the pumpdown by condensing almost any residual background gases. The magnetically operated shutter permits accurate (to $\pm \frac{1}{2}$ sec) timing of the period during which vapor is collected. It also permits a background determination by shutting off the vapor beam. A stack of 12 targets, a built-in magnetically operated target ejector, and a target storage area permit determinations to be made at a number of different temperatures without opening the apparatus. Each target is analyzed for the amount of condensate by direct weighing or, in the case of samples with extremely low vapor pressures, appropriate isotopes may be vaporized and radioactive counting methods can be used. In some cases a radioactive isotope is available for direct evaporation and counting, in other cases the condensate can be sent out for activation in a nuclear reactor and subsequently counted. All three methods have been used.

Figure 3 shows a schematic of the "Effusion-Mass Spectrometric" equipment. The method of producing the vapor beam is similar to that in figure 2. Here instead of condensing out the vapor within a mean free path of the orifice, the vapor beam passes through a collimator into the ionization region of a time-of-flight mass spectrometer. A portion of the molecules in the vapor beam is ionized by impacting with a high energy beam of electrons which passes through the vapor beam at right angles. The unionized portion of the

vapor beam continues in a straight line and is condensed on the liquid nitrogen cold finger whose function is to keep the background pressure in the instrument as low as possible. The ionized particles in the beam are extracted at right angles to both the electron and vapor beams and accelerated down a field free flight tube by means of appropriately pulsing the grids shown on the figure. The vapor beam must pass through the grids shown on the radiation shields before entering the mass spectrometer. These grids are impressed with opposite polarities in order to prevent most of the stray electrons from the cell heating source, and also any positive ions formed in the region around the effusion cell by any process, from entering the mass spectrometer. As a further precaution, a magnetically controlled shutter can be used to shut-off the vapor beam for the purpose of obtaining a background correction measurement at any time as in the simple effusion apparatus. In this program the apparatus is used primarily to obtain information about the nature of the species existing in the vapor. The simple effusion and the continuously monitored effusion methods are used to obtain absolute pressure data. However, this mass spectrometric equipment has been shown to yield quantitative vapor pressure and heat of vaporization data with large uncertainty in the former case, less uncertainty in the latter. As mentioned previously, the slope of vapor pressure vs $1/T$ is more reproducible than are absolute vapor pressures. To circumvent the problem of the unpredictable gain fluctuations produced in the electronics of the instrument, all peaks are continuously compared to a xenon or argon background peak whose absolute value is known because it is produced by a quantitatively controlled leak of the gas into the system.

Another calibration method is to continuously compare the unknown peak to one produced by an inert material, whose vapor pressure vs T is known, also present in the cell. The sensitivity of the "as received" instrument has been improved by a modification of the ionization region to permit placement of the cell closer to the ionization region and by widening the collimating slits of both the electron beam and the vapor beam. The sensitivity was thereby increased by a factor of 10 to 100 with some loss of resolution. The instrument could now detect silver isotopes at equilibrium pressures of about 10^{-7} to 10^{-8} atm and resolve adjacent mass peaks at about mass 200. High speed differential pumping has been added to the effusion cell and ionization regions in order to reduce background, pump-down time, and to permit the study of species arising from the interaction of materials with reactive gases being bled into the effusion cell. In practice, it has not been possible to obtain useful results with electron energies below about 12 ev in spite of the fact that the electron energy is continuously variable between 0 and 100 ev. Accurate appearance potentials down to low electron energy have not been seriously attempted for this reason.

Figure 4 shows a schematic diagram of the apparatus used for monitoring continuously the weight of a vaporizing sample and the force exerted by the vapor particles effusing from a cell orifice. The basic method is well known. The advantage of this device over its previous counterparts is the fact that data taking has been made highly automatic. The sample is hung from one arm of a highly sensitive analytical balance and radiantly heated by means of a resistance furnace. A magnet coaxial with a stationary solenoid is attached to the arm of the balance. The force exerted by the sample is determined by calibrating the force between the solenoid and the magnet in terms of the current flow in the solenoid. Thus the balance never leaves the null position and only the solenoid current is measured by the voltage drop it produces across a series resistor. The voltage is read by a suitable recording potentiometer thus producing a weight vs time trace. The solenoid current is controlled to hold the null position by virtue of the fact that any movement of the balance arm due to changing forces exerted by the evaporating sample is sensed by coils of a linear variable differential transformer. The displacement of its rigidly mounted core from the null position produces an error voltage and a phase change in the transformer secondaries

which are respectively related to the magnitude and direction of the displacement. As a result of this phase and voltage signal, a servo drives a potentiometer to vary the amount of current flowing through the solenoid windings. Thus, much of the tedious changing of weights and data recording are largely eliminated.

Figure 5 shows a schematic diagram of the null point torsion effusion apparatus developed under this program. Again the basic principles of operation are well known and the most attractive feature of the equipment is its automation. However, in this case a few more fundamental benefits have been obtained. In the past versions of this type of equipment the experimenter was plagued by frequent calibrations because of changes in the torsional constant of the wire from hysteresis, thermal cycling, and simple changes in the torsional constant with temperature because the wire extended into the furnace hot zone. Also the wire material and/or diameter had to be changed frequently in order to stay within a given angular displacement and a desired accuracy for various pressure ranges. Generally the pressures to be measured can vary over 2 or 3 orders of magnitude, so a wire must be selected with a torsional constant that will yield a measurable deflection at the lowest pressure yet remain on scale for the highest pressures measured. Only a fraction of the total possible rotation of the cell is normally measurable with most equipment. In the equipment under discussion these difficulties are virtually eliminated. The usual type of cell is attached to a rather long rigid bar which in turn is suspended from a fine wire which possesses as low a torsional constant as possible consistent with the strength necessary to carry the weight of the assembly. This wire is then attached to a micrometer head to facilitate positioning of the zero point. In this apparatus the wire is located at room temperature and acts only as a bearing. Its torsional constant sets the lower limit of sensitivity of the equipment. The effusion-torsion force is counterbalanced by the force produced between the solenoid, rigidly mounted to the suspended bar and effusion cell, and two fixed magnets. The latter force is proportional only to the measured current passing through the solenoid. A mirror, which is rigidly mounted to the suspension bar, reflects a beam of light coming through the sight to two photocells. As the mirror rotates it increases the amount of light falling on one of the photocells. This causes a motor to turn a potentiometer which alters the current flow in the solenoid in a manner which returns the suspension to the null point. The solenoid current can be monitored by a recorder to record vapor pressure vs time or temperature. The system is calibrated by utilizing materials of known vapor pressure. An added advantage of the magnets and solenoid is that they also act as a damping device to eliminate many of the random oscillations present in the usual torsion-effusion system.

Figure 6 is a schematic diagram of equipment utilized by the General Electric Company for Langmuir evaporation studies at extremely high temperatures. Vaporization data was obtained on some of the most refractory materials known at temperatures generally higher than attained in any previous measurement. The temperatures and materials of interest precluded the use of any known container material and therefore dictated the use of the Langmuir method. The measurements made are necessarily very time consuming and most basic in nature. The apparatus consists mainly of a water cooled quartz heating chamber. A ring shaped specimen is placed on the support wires and quickly brought to temperature by means of 25 KW induction heater. The complications entailed by the use of a radiation shield are avoided because of the large amount of power available. After the sample has vaporized at temperature for a reasonable length of time the heater is shut off and the cooled specimen is removed from the apparatus and weighed. The vapor pressure is then calculated from the Langmuir equation by simply dividing the weight loss by the time at temperature and assuming that $\alpha L = 1$. The method must be considered crude because of its simple but tedious nature. Only simple weight losses, physical dimensions, and time periods are measured and the sample has to be removed, weighed,

and reinstalled in the apparatus for each data point. This procedure thus entails considerable care and requires a large amount of pump-down time. Also for the materials of interest the sample has to remain at temperature for appreciable time periods in order to obtain reasonable weight losses especially at the lower temperature ranges. Temperatures are measured by sighting an optical pyrometer on 4 black-body holes drilled circumferentially around the ring and correcting for window transmission. The effective temperature for any run is taken as the arithmetic average of all measurements during the run. Gradients of $\pm 20^\circ\text{K}$ were typically encountered. It is readily seen that this method is capable of yielding the rate of weight loss in vacuum for a material as a minimum. Further, if $\alpha L = 1$ and the vapor species are known, the vapor pressure and other thermodynamic and kinetic data may be obtained. The vapor species generally are not obtainable by this method. This information was obtained by other means. The temperature ranges investigated (to 3400°K) are among the highest that have been attained in this type of work.

Figure 7 is a schematic diagram of the matrix isolation apparatus constructed by G.E. which is used to determine the identity and structure of high temperature vapor species. The species are allowed to effuse from a Knudsen cell and are condensed simultaneously with a stream of inert gas, introduced by the matrix line, on a liquid helium cooled window. The attempt here is to "freeze in" the high temperature molecule in its existing configuration for later study by infrared absorption techniques. In general a large number of molecules are needed for infrared studies and several hundred times this amount of inert gas is needed to form an effective matrix. The Knudsen cell is heated inductively and after a sufficient density of the matrix-molecule deposit has been built up, the gas flows are interrupted and the window is rotated parallel to the other two windows shown. The infrared absorption spectrum of the deposit is then obtained and examined. The method though promising is as yet not too well established and is plagued with numerous experimental difficulties. Aside from the problems associated with the use of a Knudsen cell itself there is the considerable difficulty and expense of working with liquid helium. The effusion cell must be extremely well shielded. There is some difficulty in the interpretation of the resulting data since the matrix has been found to interact with the trapped molecules and thereby shift its fundamental absorption frequencies. The shifts have been explained qualitatively in a few cases but much more work remains to be done. For example there is some evidence that migration and subsequent reaction in the matrix even at liquid helium temperature, may alter the nature of the original species formed in the high temperature vapor. The technique has promise in that a measurable number of molecules can be obtained at temperatures significantly lower than normally necessary in other methods and that the spectra obtained are generally less complex. The lower temperatures also make the container problems less acute. This method should prove to be a valuable supplement to the information currently being obtained by means of optical and microwave spectroscopy and also electron diffraction.

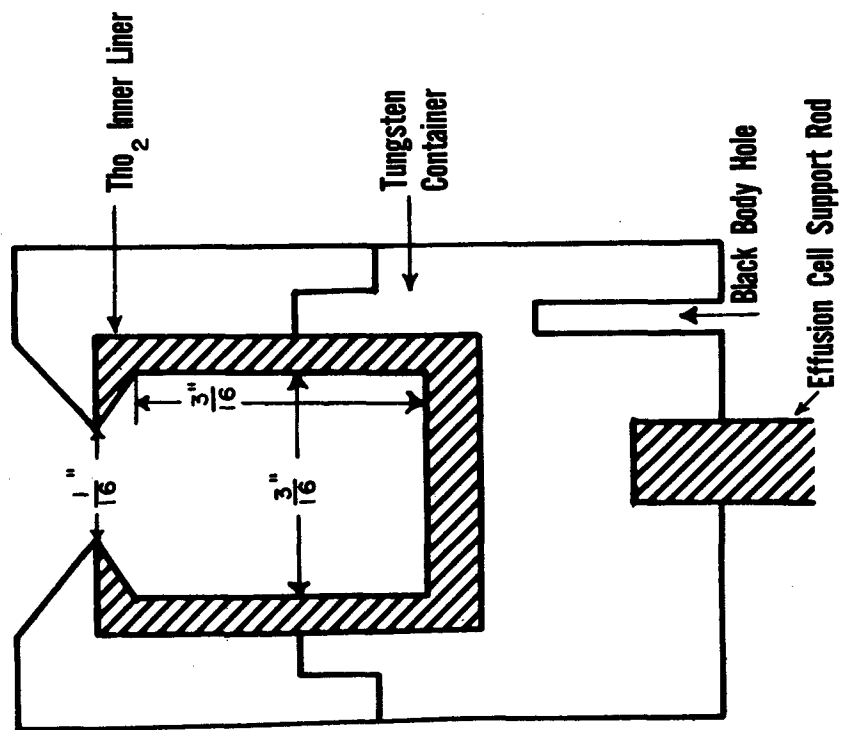
As indicated by the above description of the methods and currently used equipment, it is evident that much work remains to be done even before an understanding of many of the most basic elements of high temperature vapor pressure measurements will be obtained. In particular much ingenuity will be required in the future in devising experiments which will shed light on the nature of the various α 's of interest in vaporization studies, applicability of the cosine law, influence of orifice size and shape, sorption effects on equilibrium attainment at low vapor pressures in cells, electron impact cross-sections, photo and thermal ionization effects and pseudo-equilibrium situations. Methods for improving the accuracy and the ease of data taking should be developed. And last but not least, entirely new methods for the determination of vapor pressures and vapor species should be sought for, which do not have some of the disadvantages of methods presently in use.

BIBLIOGRAPHY

The following reference material contains excellent bibliographies and direct information on vapor pressure measurement as discussed in this paper.

1. Proceedings of an International Symposium On "High Temperature Technology", 1959, McGraw-Hill Book Co., Inc., New York.
2. Proceedings of the Symposium on "High Temperature - A Tool For The Future", 1956, Stanford Research Institute, Menlo Park, California.
3. WADD TR 60-463, Part I, Contract AF 33(616)-6840
4. WADD TR 60-646, Part I, Contract AF 33(616)-6841
5. Brochures 6-60-1, 6-60-2, 6-60-3, Nuclide Analysis Associates, State College, Pennsylvania.
6. Bulletin MS-6, Bendix Corporation, Cincinnati 8, Ohio.
7. Argonne National Laboratory Report, ANL-6156, 1960.

EFFUSION CELL NO. 1



EFFUSION CELL NO. 2

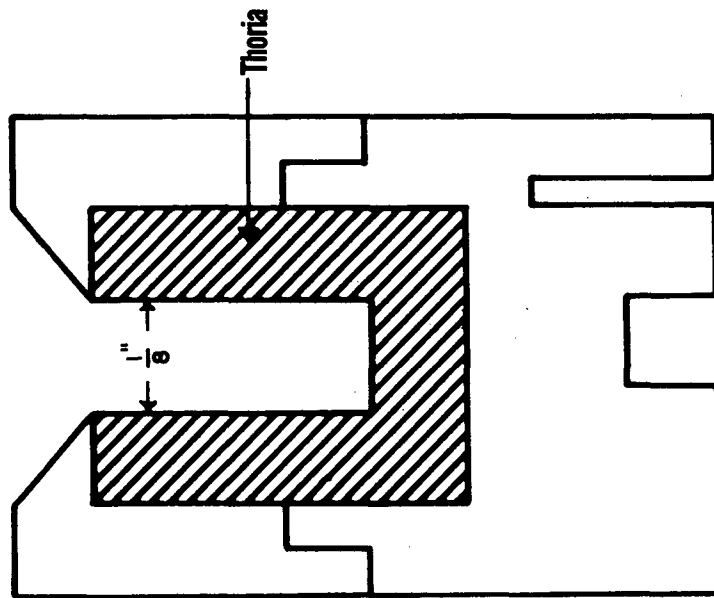


Figure 1.

SCHEMATIC DIAGRAM OF THE SIMPLE EFFUSION APPARATUS

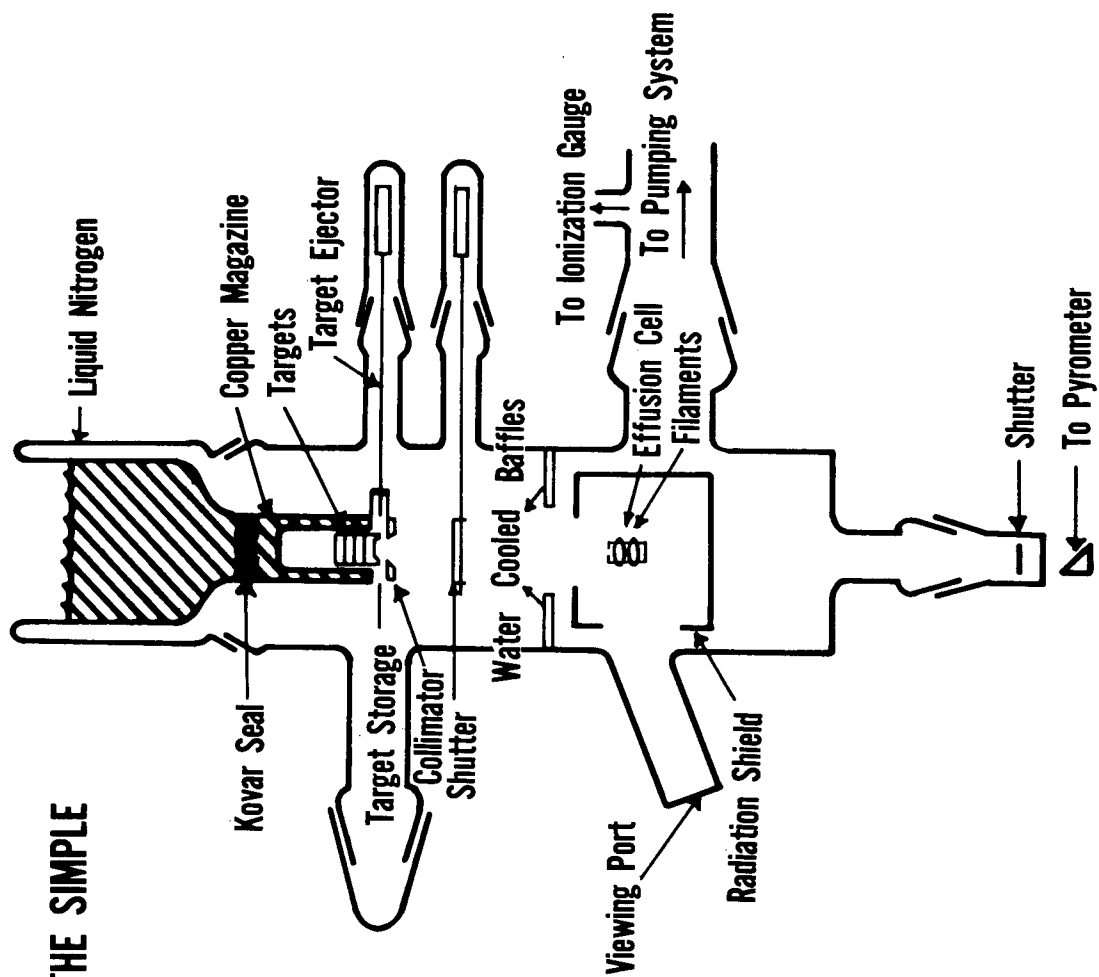


Figure 2.

THE EFFUSION - MASS SPECTROMETRIC SET-UP

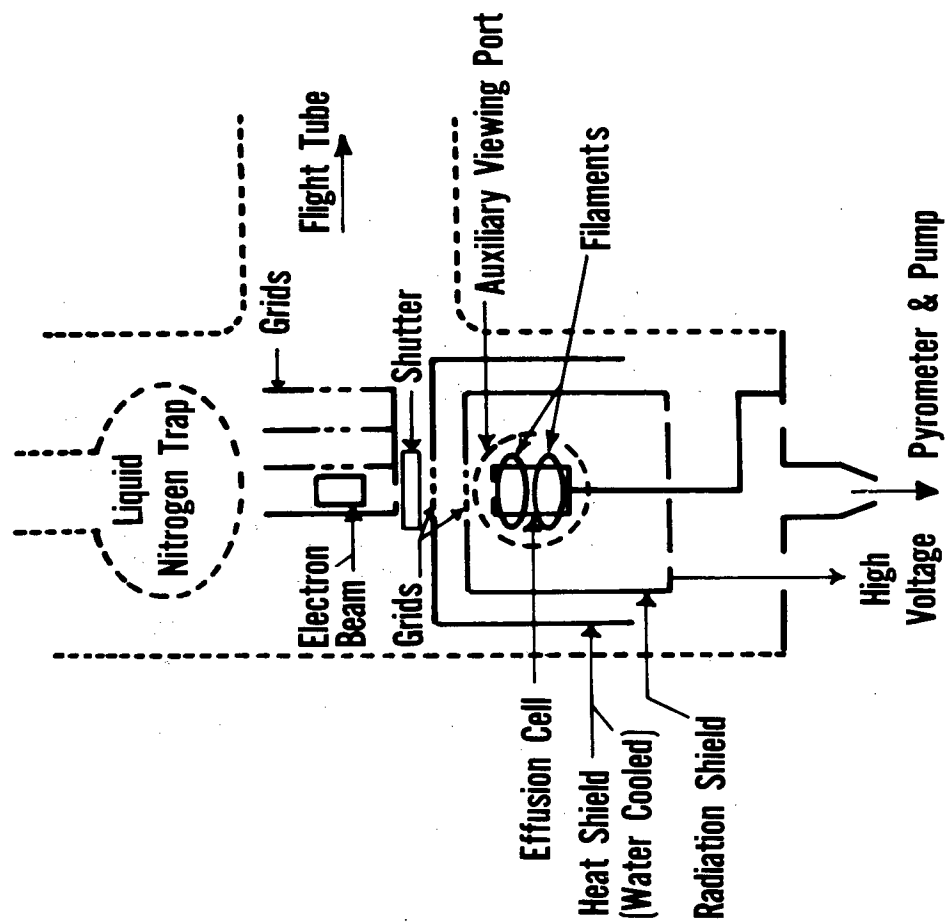


Figure 3.

CONTINUOUSLY MONITORED WEIGHING DEVICE

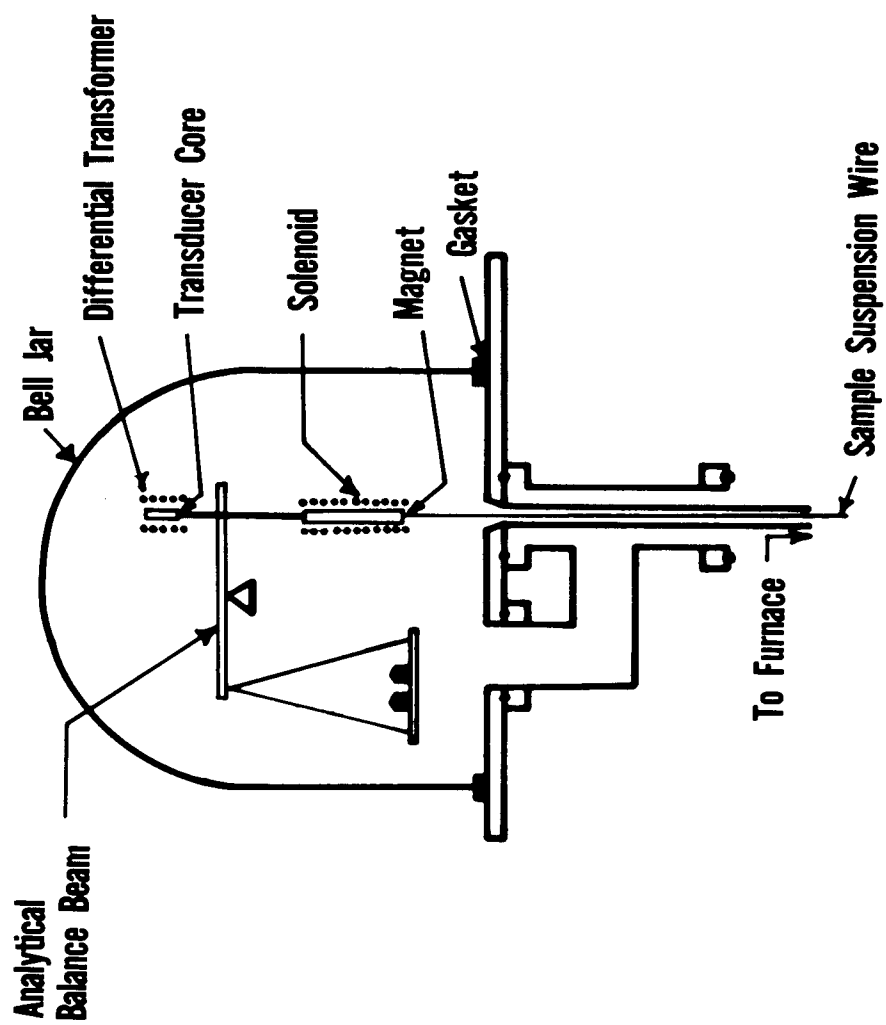


Figure 4.

NULL-POINT TORSION EFFUSION APPARATUS

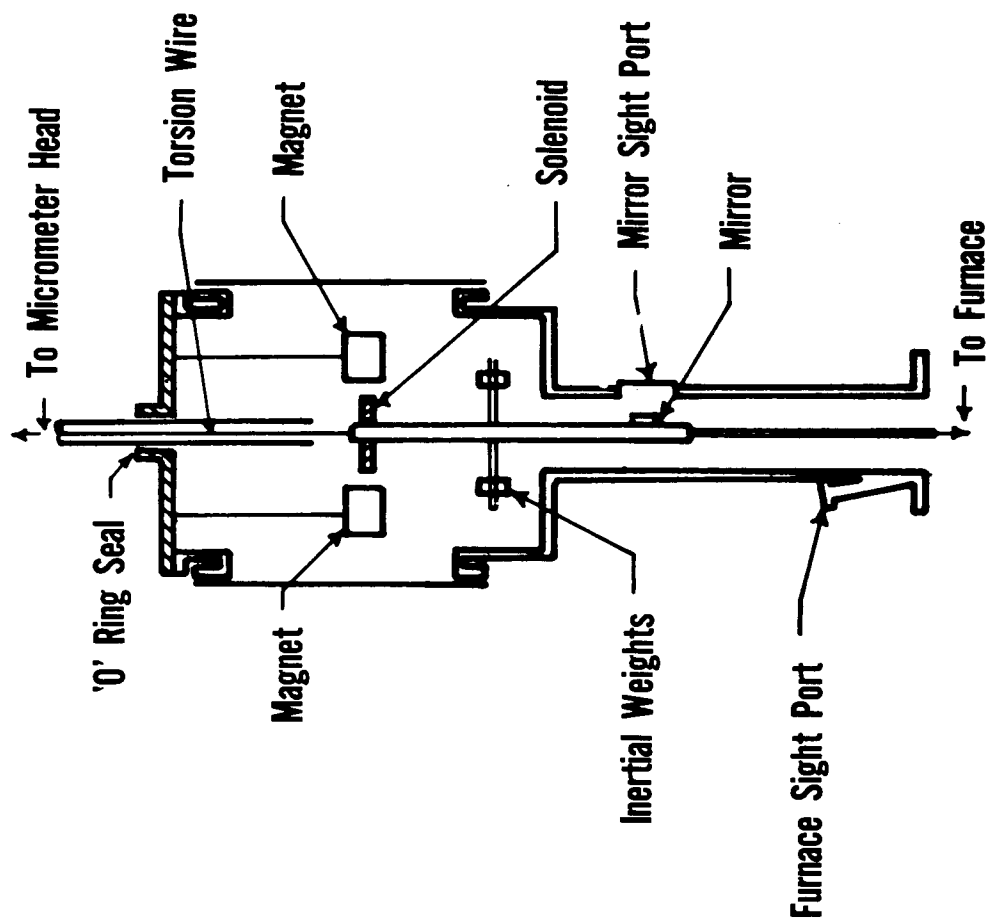


Figure 5.

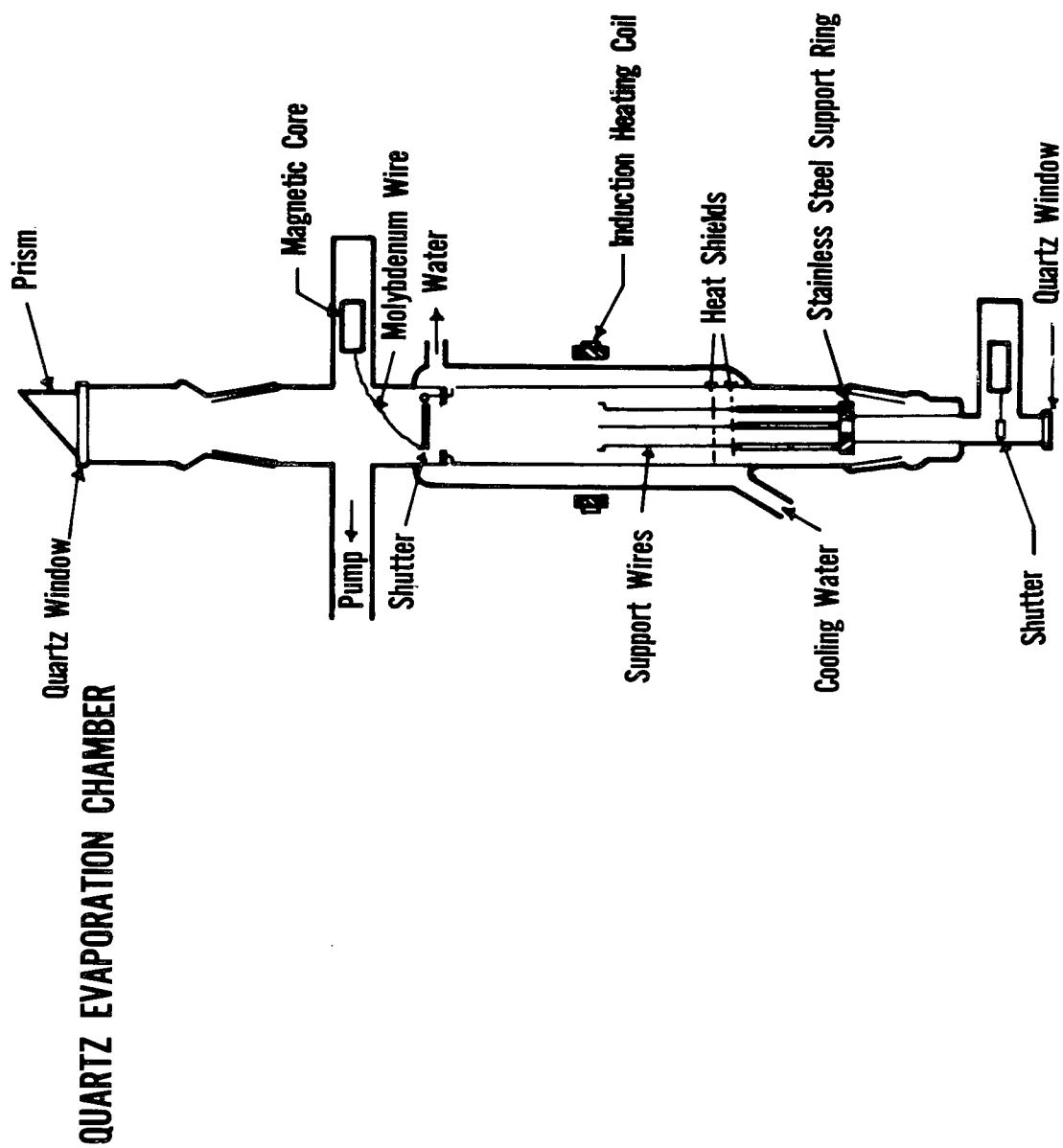


Figure 6.

EQUIPMENT FOR MATRIX ISOLATION STUDIES

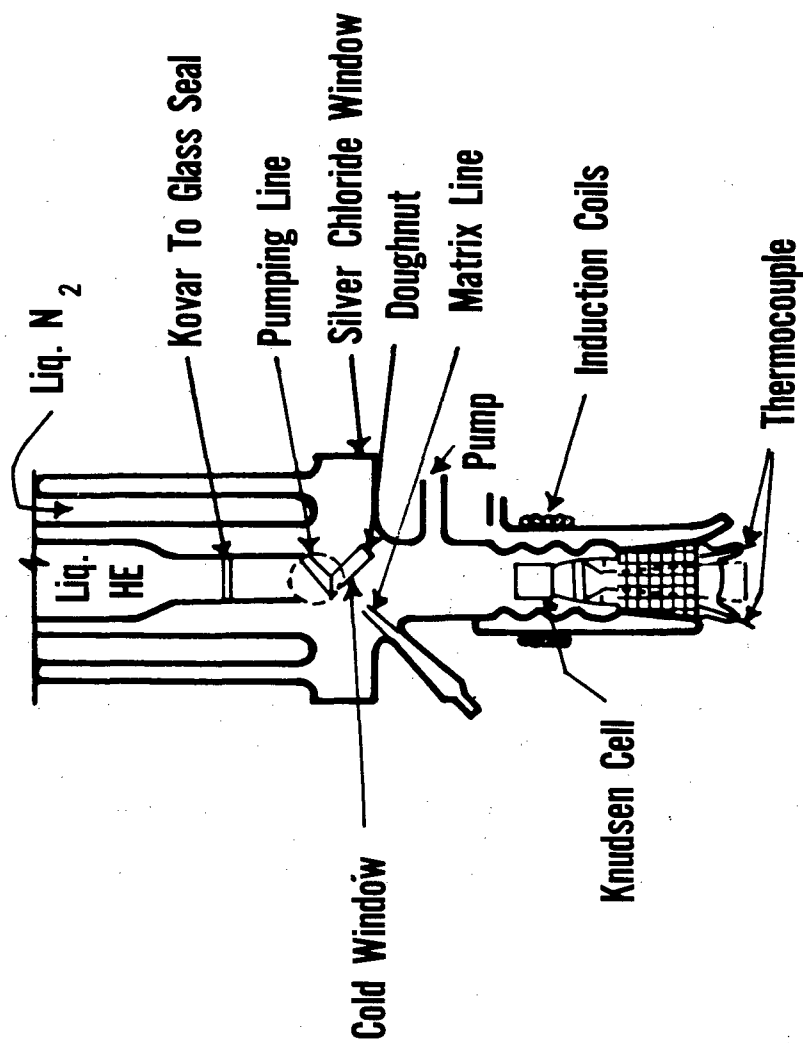


Figure 7.

THE THERMODYNAMICS OF ABLATION

Dr. Emile Rutner

Directorate of Materials and Processes, ASD

Introduction

The rate of heat transfer between fluids and solid bodies at high temperature and high heat fluxes usually depends not only on the transport properties, heat flux, initial temperature of the system, and flow conditions, but also on any combination of the following processes: sublimation, fusion, vaporization, chemical reactions at the interfaces, decomposition of the solid body below the surface, and the flow behavior of any liquid or glass film which may exist or be formed during the heating process. The prime example illustrating all these processes, and one involving all these factors is that of ablative cooling. This phenomenon will be discussed with the idea of illustrating the type of transport and thermodynamic data required for determining the rate of ablation of a given system as a function of heat flux.

In outlining the problem we will assume that a heat flux is flowing across a gas boundary layer to the surface of the solid body. The origin of this heat flux may be aerodynamic heating as in the case of a nose cone, or it may be due to the presence of a preheated flowing stream as in the case of a rocket nozzle. Figure 1 illustrates the system being considered. This system has been treated in various degrees of generality by Scala (1), Sutton (2), Sutton and Scala (3), Lees (4), Adams and Bethe (5). Our discussion will be limited to a review of their results. The most general problem involves two fluid boundary layers (see figure 1): the gas-solid (or gas-liquid) layer and the liquid-solid layer. The best way to treat the problem is to separate the interaction of the two interfaces. Relations as expressed in equations 1 to 5 are the same for both the gas-solid and the gas-liquid layers and may be applied to either, but for purposes of discussion we will consider them only as they apply to the interaction of the gas-solid interface. The equations are first listed and then a discussion is given of the techniques for evaluating the quantities necessary to solve the problem.

The Gas-Solid Interface

Gas-Solid Interactions

Equation 1 represents the conservation of specie, i , in a system of n species and for which $n-1$ such equations are required.

$$\rho u \frac{\partial c_i}{\partial x} + \rho v \frac{\partial c_i}{\partial y} = \frac{\partial}{\partial y} \left(\rho D_{i1} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) + w_i \quad (1)$$

where

- c_i = mass fraction of species.
- ρ = density.
- u = x component of gas velocity (see figure 1).
- v = y component of gas velocity (see figure 1).

$$\rho u \frac{\partial c_i}{\partial x} = \text{convective concentration change in the x direction.}$$

$$\rho v \frac{\partial c_i}{\partial y} = \text{convective concentration change in the y direction.}$$

$$\frac{\partial}{\partial y} \left(\rho D_{ij} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) = \text{concentration changes due to normal and thermal diffusion, respectively.}$$

D_{ij} = binary diffusion coefficient.

D_i^T = thermal diffusion coefficient.

W_i = rate of change of concentration of specie, i, due to chemical reaction.

Mass continuity is expressed by

$$\frac{\partial}{\partial x} (\rho u r_o^n) + \frac{\partial}{\partial y} (\rho v r_o^n) = 0 \quad (2)$$

which states that the total mass is conserved.

Equations 3 and 4 represent the conservation of momentum

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial v}{\partial y} = - \frac{\partial P}{\partial x} + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (3)$$

$$\frac{\partial P}{\partial y} = 0 \quad (4)$$

where

$$\rho u \frac{\partial u}{\partial x} = \text{convective change in momentum in the x direction.}$$

$$\rho v \frac{\partial v}{\partial y} = \text{convective change in momentum in the y direction.}$$

$$\frac{\partial P}{\partial x} = \text{pressure gradient in the x direction.}$$

$$\frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) = \text{effect of viscosity on the momentum.}$$

Equation 5 represents the conservation of energy.

$$\begin{aligned} \bar{c}_p \left(\rho u \frac{\partial T}{\partial x} + \rho v \frac{\partial T}{\partial y} \right) = & u \frac{\partial P}{\partial x} + \mu \left(\frac{\partial u}{\partial y} \right)^2 + \frac{\partial}{\partial y} \left(\kappa \frac{\partial T}{\partial y} \right) \\ & - \sum_i w_i h_i + \sum_i (c_p)_i \left(\rho D_{i1} \frac{\partial c_i}{\partial y} + D_i^T \frac{\partial T}{\partial y} \right) \frac{\partial T}{\partial y} \quad (5) \end{aligned}$$

where

$$\bar{c}_p = \sum_i c_i (c_p)_i \text{ or the mean heat capacity.}$$

$$(c_p)_i = \left(\frac{\partial h_i}{\partial T} \right)_p \text{ or the heat capacity of specie, i.}$$

$$\bar{c}_p \left(\rho u \frac{\partial T}{\partial x} + \rho v \frac{\partial T}{\partial y} \right) = \text{convective heat transfer.}$$

$$h_i = \text{enthalpy of specie, i.}$$

$$u \frac{\partial P}{\partial x} = \text{change in kinetic energy due to pressure gradient.}$$

$$\mu \left(\frac{\partial u}{\partial y} \right)^2 = \text{change in kinetic energy due to viscous loss.}$$

$$\frac{\partial}{\partial y} \left(\kappa \frac{\partial T}{\partial y} \right) = \text{change in energy due to heat conduction.}$$

$$\sum_i w_i h_i = \text{total heat evolved by chemical reaction.}$$

$$\sum_i (c_p)_i \left(\rho D_{i1} \frac{\partial c_i}{\partial x} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \frac{\partial T}{\partial y} = \text{energy transfer due to both normal and thermal diffusion.}$$

Behavior of the boundary layer is specified by the equation of state, assumed here to be the perfect gas law

$$P = \frac{\rho RT}{\bar{M}} \quad (6)$$

$$\bar{M} = \sum_i x_i M_i \quad (7)$$

where

P = pressure.

R = gas constant.

\bar{M} = mean molecular weight of the boundary layer.

x_i = mole fraction of specie, i .

M_i = molecular weight of specie, i .

The Binary Transport Coefficients

Note that the quantities necessary to complete the expression for equation 1 were the rate of reaction, W_i , and the diffusion coefficients, D_{ij} and D_i^T . We shall first discuss the evaluation of D_{ij} from available data. The expression for D_{ij} is given by

$$\left[D_{ij} \right]_i = \frac{B \left[\frac{T^3 (M_i + M_j)}{2 M_i M_j} \right]^{1/2}}{P \sigma_{ij}^2 \Omega_{ij}^{(1,1)} (\tau_{ij}^*)} \quad (8)$$

where

B = a constant dependent only on force laws assumed.

$\Omega_{ij}^{(1,1)}$ = a function of collision integrals (tabulated in reference 6) for various potential energy functions.

$$\tau^* = kT / \epsilon_{ij}$$

σ_{ij} and $\epsilon_{ij/k}$ = characteristic constants of the potential energy function, $V_{(r)}$.

The potential energy function, $V_{(r)}$, describes the molecular interaction as a function of the distance of separation, r , between two molecules and is most commonly expressed by

$$V_{(r)} = 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (9)$$

where

$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$, and σ_i and σ_j are the cross sections for the molecules, i and j , respectively.

$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$ and ϵ_i and ϵ_j are the root mean values of the depths of the potential wells for i and j, respectively.

In a multicomponent system containing molecules other than i and j, the binary diffusion coefficient is written as $[D_{ij}]$ and is obtained from D_{ij} as shown in reference 6. Frequently, however, D_{ij} itself, is a good approximation for $[D_{ij}]$ for each pair of molecules. In the absence of the required σ and ϵ , these constants can best be evaluated from the variation of viscosity with temperature or from Joule-Thompson coefficients (6).

Inasmuch as the transport coefficients are interdependent, they will be treated together although they appear scattered through all of the foregoing equations. The binary viscosity coefficient is related to D_{ij} by the following relation:

$$[\mu_{ij}]_1 = \frac{5}{3} \left(\frac{M_i M_j}{M_i + M_j} \right) \frac{P [D_{ij}]}{A_{12}^* R T} \quad (10)$$

The binary viscosity coefficient in a multicomponent system, $[\mu_{ij}]$, can be evaluated from μ_{ij} by the method described in reference 6. The coefficient of binary thermal conductivity, $[K_{ij}]$, is approximated by

$$[K_{ij}]_1 = \frac{25}{8} P \frac{[D_{ij}]_1}{T A_{12}^*} \quad (11)$$

A^* is approximately unity in both equation 10 and 11. All terms have now been defined.

From the above expression we can now evaluate the thermal diffusion coefficient from equations 12 and 13.

$$[d_T]_1 = \frac{\rho}{n^2 m_i m_j} \frac{[D_T^T]_1}{[D_{ij}]_1} \quad (12)$$

$$[d_T]_1 = \frac{x_i x_j}{6 [K_{ij}]_1} \frac{s_{x_i}^{(i)} - s_{x_j}^{(j)}}{Y_k + X_k} (6 C_{ij}^* - 5) \quad (13)$$

where

- n = number of molecules per cubic centimeter.
- m_i and m_j = mass of molecules, i and j, respectively, in grams per molecule.
- X_i and X_j = mole fractions of i and j, respectively.
- $s_{x_i}^{(i)}$ and $s_{x_j}^{(j)}$ = functions of thermal conductivities and molecular weights.
- C_{ij}^* = ratio of collision integral, which is approximately equal to unity.
- Y_k and X_k = functions of thermal conductivities and mole fractions.

The $[K_{ij}]_1$ is the thermal conductivity to a first degree of approximation as given by Hirschfelder (10).

From the foregoing discussion it is apparent that a knowledge of viscosity coefficients and the potential function for the molecular interaction leads to the evaluation of the

transport properties. Unfortunately, the situation in actual practice is not so simple. Viscosity coefficients have been measured only for readily available compounds and these only at moderate temperatures. For refractory oxides in the gaseous state, the only recourse would be to actual (and difficult!) experimentation or estimation from kinetic hard sphere theory. Even for such simple gases like air, experimental data is lacking.

The Term W_i

The rate of production of specie, i , in any given volume can be generally written as

$$W_i = \sum_{\ell} A_{\ell} e^{-\frac{E}{RT}} \pi [n_j]^m \quad (14)$$

This expression represents the sum total of all the number, ℓ , of reactions which produce and consume the specie, i . The summation is taken over all species, j , partaking in the reactions. The constant, A_{ℓ} , is the Arrhenius factor for the ℓ th reaction.

For a unimolecular decomposition, W_i becomes

$$W_i = \frac{dn_i}{dt} = A e^{-\frac{E}{RT}} (n_i) \quad (15)$$

E is the energy of activation, and n_i , number of particles of species, i , in a given volume.

If W_i is the result of several reactions, then

$$W_i = \frac{dn_i}{dt} = A_1 e^{-\frac{E_1}{RT}} \pi (n_i)^m + A_2 e^{-\frac{E_2}{RT}} \pi (n_i)^m + \dots + \text{etc.} \quad (16)$$

Of course, W_i involves not only the gas phase reactions, but also the reactions leading to evaporation of species from the solid or liquid surface and subsequent decompositions in the gas phase. For example, if the surface is an organic material such as Teflon, $(C_2F_4)_n$, it has been found necessary to explain the observed W_i by postulating two reactions: first, evaporation of the Teflon; and second, the gas phase reaction with oxygen.



In practice one must make reasonable assumptions about what reactions do take place and the relative contributions of each to the composition of the gas phase and the enthalpy changes in the system. For more complex refractories, this becomes difficult because of the lack of detailed knowledge of the actual species evaporating, the rates of evaporation, and the reaction enthalpies involved. For each given materials system, it is necessary to determine both the species formed and the enthalpy changes.

Conservation of Mass and Momentum

So far, we have confined ourselves to the evaluation of the conservation of species only as given by equation 1. We can now look at the conservation of total mass as expressed by equation 2. In equation 2 the symbols, ρ , u , and v , represent density and the velocity components; r_0 is the cross-sectional radius of the body; and n is a function of the body geometry, being $n = 0$ for a flat plane surface, and $n = 1$ or $n = 2$ for curved surfaces.

Equations 3 and 4, given previously, define the conservation of momentum and introduce no terms not already discussed.

Heat Capacity

The only term remaining to be discussed is the heat capacity, which appears in equation 5. When molecular data is available, heat capacities for gases are readily estimated. For example, if the vibrational frequencies of a molecule are known, the heat capacity is given by

$$c_p = A + R \sum_i \left(\frac{h_c}{kT} \right)^2 \frac{d_i \omega_i^2 e^{-\frac{\omega_i h_c}{kT}}}{1 - e^{-\frac{\omega_i h_c}{kT}}} \quad (19)$$

where

$A = 3.5R$ for diatomic and linear molecules and $4R$ for nonlinear molecules.

R = gas constant.

h = Planck's constant.

k = Boltzmann's constant.

d_i = degeneracy of the i th mode.

c = speed of light.

ω_i = vibrational frequency of i th mode in cm^{-1} , and summation is carried out over all vibrations of the molecule.

Unfortunately, the equation has shortcomings: first, usually there is little information about the molecules formed in a complex evaporation; and second, heat capacity cannot be represented by an assembly of simple harmonic oscillators at high temperatures. Under such conditions, once again recourse lies only in experimental observations.

In principle, we have demonstrated how all coefficients may be evaluated for all the foregoing equations. We must emphasize, however, that supporting data for the materials of interest in the re-entry problem are largely not available. Such data, which include the rates and types of species evaporating from a given surface, the heats of vaporization and reaction, and molecular properties of the various species, must be determined experimentally.

Correlation

Since the complexity of the equations which have been written is manifoldly increased by the necessity of solving them for a multicomponent system rather than for a simple binary system, it becomes obvious that solution of the gas-solid (or gas-liquid) interaction for real materials requires some simplifying assumptions.

Two assumptions that can be made are:

1. Thermal diffusion is negligible for many cases.
2. The composition of the boundary layer at any given point is that which corresponds to the equilibrium composition at a steady-state temperature at that point; or equilibrium is established at the gas-solid interface and the species are assumed to diffuse without further reaction into the boundary layer.

These assumptions eliminate the need for specific knowledge of reaction rates, but require knowledge of the equilibrium constants. Of course, neither aspect of assumption 2 is valid if evaporation is accompanied by decomposition of the solid. In some instances, we can assume that the change of solid to gas is irreversible but that shifting equilibrium is maintained in the gas phase. This is certainly true in the case of decomposing organic solids in an air stream.

Still further simplifications can be made for most real cases. The ablation of Teflon by interaction with an air boundary layer, for example, can be treated by assuming that the dominant chemical reactions are as expressed previously in equations 17 and 18 and that equation 17 is the rate controlling reaction at the surface. The linear recession rate for the solid can be obtained from the energy balance and the integrated mass production rate expressed for equation 17. Imposing the condition that $T = T_w$ at the surface and $T = T_0$ inside the solid. The energy balance can be expressed as

$$\frac{d}{dY} \left(K \frac{\partial T}{\partial Y} \right) + \rho \dot{Y} c_s \frac{dT}{dY} = \rho A (h_m - h_p) e^{-\frac{E}{RT}} \quad (20)$$

where

K = thermal conductivity of the gas phase.

c_s = specific heat of the solid phase.

E = activation energy for equation 17.

A = Arrhenius factor.

$(h_m - h_p)$ = enthalpy of depolymerization.

Scala (1) found that the linear rate of ablation can then be expressed as:

$$\dot{Y}^2 = \frac{K_s A e^{-\frac{E}{RT}}}{\frac{E}{RT_w} \left[1 - \frac{T_0 + \delta}{T_w} + \frac{E \delta}{RT_w^2} \left(1 - \frac{T_0}{T_w} \right) \right]} \quad (21)$$

where

$$\delta = \frac{h_m - h_p}{c_s \frac{E}{RT_w} \left(1 - \frac{T_0}{T_w} \right)}$$

K_s = thermal diffusivity of Teflon.

T_0 = bulk temperature of the solid.

T_w = wall temperature of the solid.

Note that reaction 18 affects the ablation rate only to the extent to which it determines T_w since the availability of oxygen at the Teflon surface is negligible. The oxygen is consumed in boundary layer, only a negligible amount being available at the surface.

Another characteristic quantity which can be calculated from the solution to equation 21 is

$$Q^* = \frac{\text{heat transfer to a nonablating surface at } T_w}{\text{mass ablating from the surface at } T_w} \quad (22)$$

This definition gives a convenient measure for the heat of ablation

$$Q^* = \left[\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w + (h_w - h_s) \right] \quad (23)$$

where

$$\begin{aligned} \dot{m} &= \text{rate of mass ablation} \\ \bar{Q} &= \text{heat transfer to the actual solid across the interface.} \\ h_w &= \text{enthalpy of the gas phase at the wall.} \\ h_s &= \text{enthalpy of the solid at the wall.} \end{aligned}$$

To evaluate h_w properly, the gas composition must be known which, in turn, requires a knowledge of the surface temperature and \bar{Q}_s at the interface, which can be determined for the quasi-steady state condition by numerical techniques. In principle, then, we have a method for evaluating Q^* , $\Delta \dot{m}$, and T_w .

As noted before, all these quantities depend critically on the knowledge of high temperature thermodynamic and transport properties. Moreover, a knowledge of the kinetics of "evaporation" or gasification must also be known if correct use is to be made of the thermodynamic properties. The problem of calculating Q^* , of course, in turn involves evaluating the effects of aerothermodynamic parameters such as stagnation enthalpy, pressure, and the composition of the boundary layer.

Experimentally, Q^* is determined by measuring the rate of mass loss, \dot{m} , at a given surface temperature and stagnation enthalpy, and measuring the heat transfer rate to a copper calorimeter from a boundary layer at the same stagnation enthalpy and wall temperature.

$$Q^* = \frac{\dot{Q}_{col}}{\dot{m}} \quad (24)$$

The Liquid-Solid Interface

All the foregoing discussion has been limited to determining the change in the heat transfer rate due to mass transfer into the boundary layer from a vaporizing surface.

In the general case of ablation the effect of the liquid-solid boundary layer should also be considered (see figure 1). A set of equations for the liquid-solid boundary similar to equations 1 to 5 can be written and solved. This discussion will be restricted to stating the effect of ablative melting on Q^* .

The expression for Q^* , when ablative melting is considered, can be written as

$$Q^* = \frac{\dot{Q}_{cal}}{\dot{m}_{total}} = f \left[\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w + (h_w - h_s) + \frac{(1-f)}{f} (h_l - h_{so}) \right] \quad (25)$$

where

f = fractional loss of material from a given surface due to gasification and vaporization.

h_{so} = enthalpy of the cold solid (interior).

h_l = average enthalpy of the liquid (which for thin layers may be taken as equal to the enthalpy of the liquid at the gas-liquid interface).

h_w = enthalpy of the gas at the gas-liquid interface.

$\Delta \dot{m}$ = mass ablation rate at the gas-liquid interface.

$\Delta \bar{Q}$ = heat transfer rate to the liquid at the gas-liquid interface.

In the above expression, $\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w$ and $(h_w - h_s)$ contribute only a fraction, f , to Q^* , while $(h_l - h_s)$, which represents the heat carried away by the flow of the liquid layer, contributes the remainder.

The problem reduces itself to the determination of the flow behavior of the liquid, which is governed by its viscosity under a given set of stagnation conditions, including the shear stress on the liquid layer. For a viscous liquid, the last term of equation 25 may be a steep function of temperature since viscosity varies exponentially with temperature. The variation of f with surface conditions for a number of systems, such as silica, has already been calculated (5,6) and found to be determined in most cases by the values for $\left(\frac{\Delta \bar{Q}}{\Delta \dot{m}} \right)_w$ and $(h_w - h_s)$.

Conclusion

We emphasize, in conclusion, that if evaporation is at high temperature, a knowledge of thermodynamics, transport properties, and kinetics would greatly aid in calculating the value of Q^* . Such information is at present required for many systems now being considered, i.e., organic solids and refractory materials. The only type of information now available, to a limited extent, for refractory materials are heat capacities, heats of formation, and heats of evaporation. Unfortunately, enthalpies and heat capacities of solids at high temperatures can best be obtained by direct measurements. In contrast, transport properties of gases at high temperatures, can probably best be determined from some measurements of molecular interactions, which can be suitably translated into transport properties.

BIBLIOGRAPHY

1. Scala, S. M., "A Study of Hypersonic Ablation", in Conference on Plastics in Advanced Flight Vehicle Environments - WADD TR 60-101.
2. Sutton, G. W., "The Hydrodynamics and Heat Conduction, of a Melting Surface", Journal Aero Science, 25, No. 1, pp 29-33 (1958).
3. Scala, S. M., and Sutton, G. W., "Proceedings of the 1958 Heat Transfer and Fluid Mechanics Institute", Stanford University Press, pp 231-240.
4. Lees, Lester, "Proceedings of the 7th Anglo-American Aeronautical Conference", pp 344-362, (1959), American Institute of Aeronautical Sciences, New York, N.Y.
5. Bethe, H. A., and Adams, Mac C., Journal Aero Space Sciences, 26, pp. 321-328, (1959).
6. Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids", John Wiley & Sons, Inc., New York, N.Y. (1954).
7. Herzberg, G., "Molecular Spectra, and Molecular Structure", Vol. II, D. Van Nostrand Co., Inc., New York (1945).

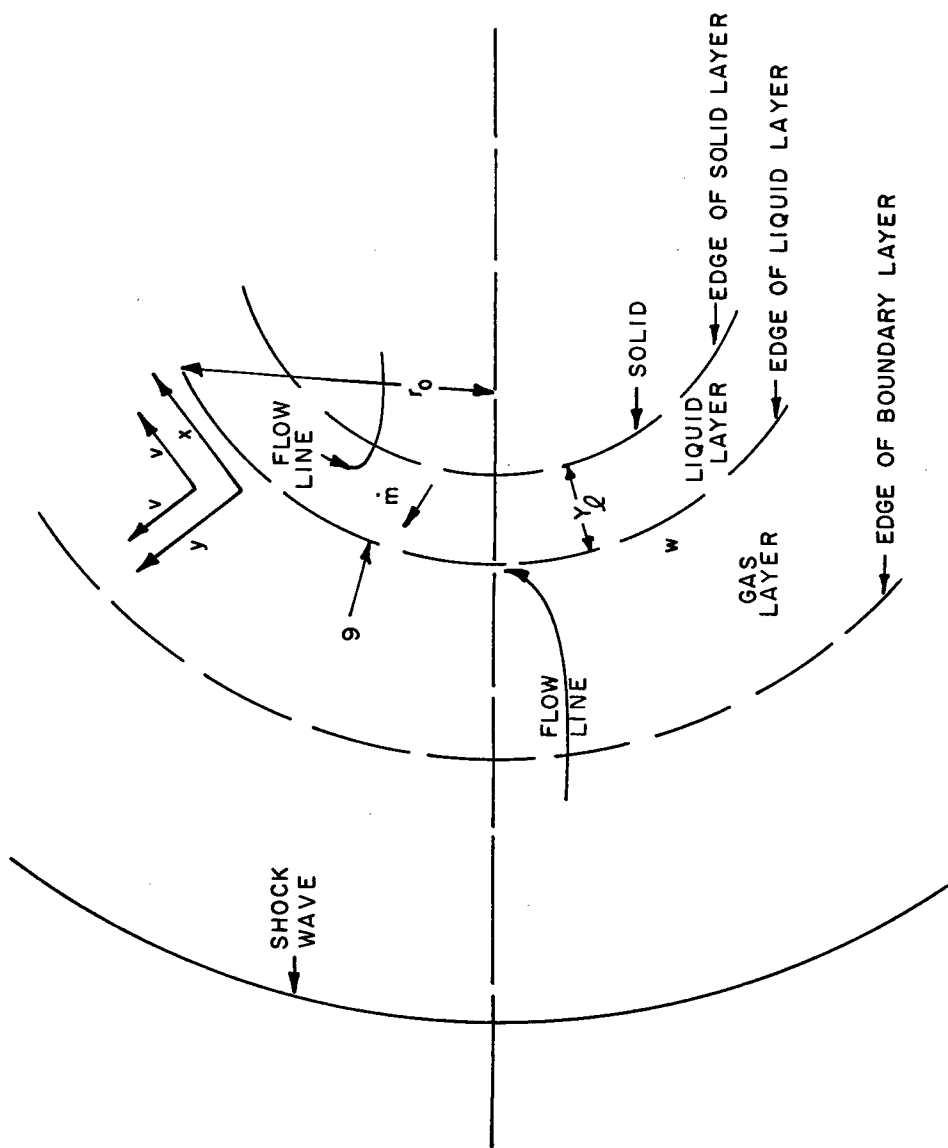


Figure 1. System of Gas Solid Interface

METEORETICS AND HYPERVELOCITY STUDIES

Alan K. Hopkins

Directorate of Materials and Processes, ASD

Introduction

Space vehicle missions of long-duration, perhaps years, make the probability of significant collision along the way with one or more meteoroids or micrometeoroids of grave consequence. The potential loss of a multimillion dollar vehicle because of this little understood hazard is sufficient justification for more extensive research.

The probability of a significant impact, one which might cause failure of a vehicle, can be determined only with data from two different sources: (1) Distribution of number, mass, and velocity of natural meteoroids over the orbit of the earth, and (2) Degree of impact damage to be expected from a wide range of particle masses, compositions, and velocities. The first can only be acquired through observations of natural bodies in space, but studies of hypervelocity impact can be performed in the laboratory.

Although knowledge concerning the environment is increasing, and it becomes possible to compute the probability of encounter with particles of various masses, the designer is still faced with the problem of determining an optimum vehicle structure to provide both mission capability and reasonable probability of survival throughout the mission. This can be solved by increased knowledge of hypervelocity impact effects of simulated meteoroids and micrometeoroids at meteoritic velocities. This paper has a two-fold purpose: one, to survey briefly the present knowledge and research completed to date of the environment as it affects the techniques employed in the acceleration of particulate matter to hypervelocities; the other, to survey the areas of significant need for continued research. Our purpose is not to concern ourselves with the specific potential materials to be used in space vehicles, but rather to gain first a complete understanding of the dynamics of hypervelocity or meteoritic impact. Once this is known, materials selection can be made logically and intelligently.

Nature of the Environment

Definition of Terminology

It is evident from the widely differing information issued by authorities concerning the number, size, density, distribution, configuration, and penetrability of meteoric materials that this field of study is new. The problem is further confused by nonuniformity in defining terms. A firm foundation for the study of the simulation of meteoric material impact effects requires a common ground for describing the space environment. The following list of definitions are those which we have accepted and will use throughout this report.

Meteoric Particle	-	A relatively small intrasolar system body or particle of any size and speed generally of cometary or asteroidal origin.
-------------------	---	---

Meteoroid	-	A meteoric particle, generally of cometary origin, of any size greater than 10^{-4} gms.
Micrometeoroid	-	A meteoric particle of less than 10^{-4} gms.
Cosmic Dust	-	Minute meteoric particles smaller than most micrometeoroids.
Meteor	-	The phenomenon resulting from the entrance into the atmosphere of a meteoric particle of sufficient mass at high speed.
Meteorite	-	A meteoric body, generally of asteroidal origin found on the earth's surface.
Micrometeorite	-	A meteorite of the approximate size of cosmic dust.
Hypervelocity	-	That velocity exceeding the speed of sound in the target material or the speed of the dilatational wave in the target.

Composition of Meteoric Material

Having defined the particulate matter found in space, we can proceed to a discussion of the relative numbers and velocity distributions of these particles as well as their composition. Meteoric particles are stony, iron or metallic masses which are smaller than many of the small planets (asteroids). Apparently they are concentrated in the ecliptic plane and move around the sun in the same direction as the planets. Large meteoric particles may be concentrated in streams irregularly placed in space. Meteorites are hard, high density materials and are the remainder of meteoric particles of large mass which have not vaporized or burned, and vary in mass from milligrams to several tons. There are three types of meteorites: siderites or metallic bodies, consisting of iron or nickel alloys; aerolites, consisting of stony materials primarily composed of silicates and oxides; and siderolites, which are iron-stone bodies. Of the three types, the metallic meteorites constitute less than 10 percent of the total.

In this paper, we shall not attempt to cover the origin of meteoric materials; however, some of the potential research outlined later will cover the determination of their origin. Most authorities agree that the bulk density of particles of cometary origin ranges from 0.05 to 0.3 gms/cc; whereas the meteoroids of asteroidal origin are as large as 8 gms/cc.

Velocity Distribution

Because of the earth's gravitational effects, material entering the earth's atmosphere cannot have a velocity of less than 11.2 km/second. Since the velocity of the earth about the sun is about 30 km/second and the maximum velocity of a meteoric particle is about 42 km/second, the maximum combined relative velocity is about 72 km/second. Secondly, in this velocity range of 11 to 72 km/second, there appears to be a distribution of velocities which varies with particle size. In addition, meteoric particle velocities vary because of time of day and month, their mean observed speed in the earth's atmosphere being highest in early morning and lowest in late afternoon.

If particles of a diameter of less than one micron tend to be blown out of the solar system by solar radiation pressure, and the ejection mechanism also depends on particle density, then to stay in the system those particles with a density of 0.05 gms/cc must have a diameter of 23 to 46 μ . However, particles .01 μ in diameter may not be affected by radiation pressure if their scattering power is low. The interplay of the gravitational effects and radiation pressure of the sun determine whether these minute particles will be spiraled onto the sun or blown out of the system. Figure 1 shows a distribution of meteor velocities as determined by radio methods during a 15-month study during 1948-1950. (1, 2) The smallest particles observable by radio methods have a mass ranging from 10^{-4} to 10^{-6} gms and their average velocity appears to be 37.5 km/sec. We account for the zodiacal light by assuming that many smaller particles must exist having lower velocities. Therefore, the average of 37.5 km/sec is probably high and should be reduced to between 28 and 35 km/sec.

Particle Distribution

The frequency of particles in the vicinity of the earth can be determined from the intensity of zodiacal light reflected by minute dust particles. A flux density of 10^{-6} particles/cm²/sec of particle radii between 1 and 10 μ (10^{-11} gms) is necessary (3) to produce zodiacal light. The frequency of particles having mass greater than "m" entering the vicinity of the earth/sq m/sec is, according to Broyles, $F_{>m} = \alpha m^{-\beta}$, where α and β are constant (4). Figure 2 depicts this mass distribution and from this curve one may infer the relative probability of impacts on a space vehicle.

The amount of satellite and rocket data taken to date tend to substantiate the mass distribution curve of Broyles. There exists a large concentration of meteoric particles in the vicinity of the sun. Zodiacal light measurements indicate that a maximum particle density between the earth and the sun occurs in the ecliptic plane. In addition, dust concentrations are expected to occur within the gravitational fields of the planets and moon and vary inversely with the 1.5 power of their distance from planet centers.

Meteoric Impact

The hazard from meteoric material impact to space vehicles can be divided into two problems: (1) surface erosion by dust particles, and (2) penetration and puncture of skins by more massive bodies.

Surface erosion has as a major consequence the reduction of thermal control since the physico-optical properties of the surface may be changed by erosion. Another consequence is that of increased drag from air friction on the roughened surface and the resultant overheating of the vehicle skin upon re-entry into the earth's atmosphere.

The consequence of puncture to a manned vehicle is obvious in view of its required pressurization, but damage may also be disastrous to internal components either from puncture by the primary impacting particle or by spalled skin material.

The problems to be solved are similar in that they both involve impact at velocities in excess of those presently obtainable in the laboratory. Two mechanisms are responsible for changing the character of the impact process at high velocity vs that occurring at low velocities.

Since momentum effects are linearly dependent upon velocity, they will dominate the low velocity experiments. Energy depends upon the square of the velocity and therefore energy effects will be predominant at high velocities. At high velocity, target materials are more resistant to momentum effects since the greater inertial stress of the target atoms dominate the common static stress of the target material at high rates of strain (5). At the maximum laboratory velocities presently obtainable, the shape of the crater in the target, resulting from impact, bears small relation to the incident particle momentum of the impacting body. We know, however, that the shape of the crater becomes slightly elliptical and that the penetration decreases as the incident particle deviates from the target's head on impact.

Impact Effects

1. Low Bulk Density Projectiles -- The probability of impact by low bulk density projectiles will be greatest because of their relative numbers, and will include predominately particles of cometary origin. Since the low density (0.05 gms/cc) particles have low cohesive strength, the major concern is the surface erosion caused by the impact of these particles on skins, mirrors, reflectors, windows, radar and infrared gear, energy collectors, thermal protection and heat balance systems.

Because of its low mass and resulting low kinetic energy, such a particle will probably fly apart upon impact and transmit only a very small portion of its original kinetic energy into the target. The most probable effects would be many small holes of slight penetration and deposition of material on the surface of the target. A dust particle $10\ \mu$ in diameter with density of 0.05 gms/cc and velocity of 30 km/sec has an incident kinetic energy of about 2×10^{-5} joules, which will be dissipated in the outer layers of the target.

2. High Density Meteoroids -- Meteoroids of asteroidal origin are generally high density materials. Impacts from these particles will occur with less frequency than those from dust particles but will produce catastrophic effects due to their high kinetic energy. A particle weighing 0.5 gms traveling with a velocity of 30 km/sec possesses a kinetic energy of about 2×10^5 joules. This amount of energy cannot be dissipated completely in the outer shell of the vehicle. Let us analyze the energy partition in the target. Figure 3 shows a representative cross section of a particle impacting on the target and gives an idea of the manner in which the energy is partitioned in the target material.

3. Phenomena Associated with High Energy Hypervelocity Impact

a. Light Emission -- Upon impact, the initial effect is the explosive removal of both target surface material and a portion of the particle material. This matter is partially vaporized, liquified, and removed as solid material. A major portion of this energy is converted into radiant energy and can be seen as the luminosity associated with the impact. The matter which does not completely leave the target surface forms the crater lip.

b. Penetration -- The kinetic energy of the impacting particle is higher than the sublimation energy of most metals. Consequently, a meteoroid with high velocity penetrates into a metal as if it were a liquid and continues until the meteoroid atoms lose enough energy to be in the range of the binding energy of the metal lattice. There are several theories at present which attempt to predict the depth a particle will penetrate a given material as well as the volume of the resultant crater. Perhaps the most widely quoted equations for making these predictions are those set forth by Kornhauser (6). Changes are reflected in the curve of figure 4 as crater volume per unit energy becomes

a function of target parameters as given by Partridge (7). The slope of the line in a graph of crater volume vs energy of the projectile will be different for different target materials depending on the modulus of elasticity or strength modulus of the material. All of the theories that have thus far been developed have dealt with velocities below 7.5 km/sec and therefore say nothing about the effects at expected meteoroid velocities.

c. Spallation -- Meteoric material penetrates a surface at hypervelocities and the Mach number at which this is done is determined by the acoustical properties of the target. The meteoric particle is preceded by a shock wave of high strength. As the energy of the shock wave is transferred to the target atoms within the shock cone, the atoms participate in the bulk motion and attain extremely high temperatures and vaporize. The vaporized atoms in the shock cone then attain velocities in the sonic region. The lattice energy of the target may be neglected and the energy of the vaporized atoms is carried forward into the skin by a compressional wave to an extent dependent upon the elastic properties of the target material. These compressional waves will be reflected as tension waves from the discontinuity at the reverse side of the structure.

At this point the analysis becomes somewhat complex and uncertain since the breakup at the surface, or spallation, depends upon the tensile strength, the existence of faults, cleavage planes, and in general the crystalline properties of the material. The spalled material will have a certain kinetic energy imparted to it which depends upon the strength of the compression wave as well as upon the other factors mentioned above which also contribute to the production of spallation. If the kinetic energy of the spalled material is sufficiently high, these secondary particles may produce damage upon impact with internal components in the vehicle.

d. Vibration -- The impact of massive meteoric particles can induce vibrations within the target materials. The amplitude of these vibrations may be sufficiently large to spall or flake off thermal coatings or may even crack open welded joints in the structure.

At present there are experimental and theoretical programs in progress to study existing laws and establish new laws of hypervelocity impact. A considerable variation exists in the equations proposed to describe these phenomena. Henderson and Stanley (8) attribute this to the following two factors:

(1). The processes which occur are extremely complex. Under low velocity conditions a small particle penetrates the target as a projectile and produces a deep hole. As the particle velocity approaches the speed of sound in the target material, something similar to transonic aerodynamic conditions occur. Penetration under these conditions depends on the rate at which the compression wave moves into the target, how efficiently the heat produced is conducted away from or melts the target-projectile combination, and some other factors not clearly understood.

(2). Experimental data, while available at relatively low speeds for large solid projectiles, are completely lacking in the range of velocities, particle size, and particle materials involved in meteoric damage. At the present time there exists essentially no data above 7.5 km/sec, which for most materials is between Mach 1 and 2. Particle sizes down to 10^{-11} gms and densities around 0.05 gms/cc are about an order of magnitude below that currently attainable in the laboratory. Therefore, the equations relating material properties, velocities, and energies have taken a variety of forms.

Experimental Observations

Despite the fact that, almost without exception, the experimental research on hypervelocity impact to date has been in the region below 7.5 km/sec, considerable work has been conducted which has resulted in large amounts of data especially in the studies of crater formations, penetrations of high density (>2 gms/cc) projectiles, surface glancing effects, and target surface erosion from gases and shattered particulate materials. Let us now briefly review some of the work accomplished in these areas.

Crater Formation

The two primary studies of hypervelocity impact have been in the area of cratering and penetrations. Gehring (9) has analyzed the dynamics of crater formation using high speed photography to watch the qualitative features of the impact. From the data obtained from these photographs, he postulated equations for the impact dynamics and determined the portion of energy partitioned from the particle to form the crater. Others who have conducted research in this specific area include those listed in references 10 through 13.

Penetration Studies

Penetration studies have constituted the principal work in hypervelocity. Research has run the gamut from qualitative studies of observing just what occurs upon impact to those of quantitative determinations of crater volume and particle penetration depth both as a function of particle energy and material and of target material and configuration. Nearly all of the work has been conducted using Metal projectiles impacting on metal or lucite targets. Only recently has tentative data been disclosed in which borosilicate glass beads were employed as projectiles (14). These projectiles more closely approximate the stony meteoritic materials in density. Data is essentially nonexistent on the effects of "puff-ball" impacts.

The one bright spot in all the research conducted to date is that most crater volume-energy relationships agree, i.e., that the volume exhibits a linear dependence upon the kinetic energy of the projectile. The exact dependence is not firm but appears to be related to the modulus of elasticity or strength modulus of the target material.

Characteristics of penetration of particulate matter into a target are not so readily defined. Summers and Charters (15) have shown that the penetration of metal particles into metal targets can be expressed in terms of the densities of the particle and target, the particle velocity, and the speed of sound in the target. Atkins (16) indicates that as craters become hemispherical and energy/volume becomes constant, the penetration is proportional to the $2/3$ power of impact velocity. James and Buchanan (17) show a linear dependence of penetration on the root reciprocal of target density. Investigators have been proving the dependence of penetration of a projectile on various physical properties of the target and of the projectile itself, but there appears to be a need for correlation of data to arrive at a unified penetration equation.

Surface Erosion

Aside from the examination of surfaces of recovered vehicles, research in the area of surface erosion has been scarce. Other than the data presented by Kornhauser (18) which is experimental data on surface roughening, and that of Beard (19) which is a theoretical treatment of the problem, the reports in the open literature are essentially nonexistent. Probably the greatest single obstacle to achieving hypervelocities for experimental

purposes is that of particulate shattering prior to impact. The cohesive forces on a particle in most cases cannot withstand the extremely high acceleration rates required to obtain hypervelocity within a reasonable distance. However, in surface erosion studies, this problem of shattering may be ignored if by utilizing modern high speed photography we identify the particles prior to impact and associate a given crater with a known fragment of the projectile. Very recent velocities in excess of 11 km/sec attained in the laboratory promise that the dynamics of surface erosion may soon be analyzed.

Spallation

Although most experimenters employing thin targets have seen spallation occur, there is a complete lack of data relative to the characteristics of the spalled material. Prior to developing a mathematical representation of the phenomenon of spallation, Maiden, et al. (20), are presently studying, quantitatively, the compressional wave propagation in target materials.

Oblique Impact

Depth of penetration and the shape of the crater produced by a particle impacting on a target can vary with the angle of incidence of the particle, as well as with its velocity. As velocity of the impacting particle increases, dependence upon the angle of incidence decreases, within small angles, because of the predominance of energy over momentum. However, the more nearly parallel the direction of the projectile is with the surface of the target, the less likely there is to be any impact effect, regardless of the speed of the projectile. The results of Culp's experiments (21) show that eccentricity decreases with increasing velocity at fixed angles of incidence. Bryan (22) has attempted to set up a model of oblique impact which can be used as a starting point in describing the phenomenon associated with this type of impact. Figure 5 shows the difference between head on and oblique impact.

Experimental Techniques

In all the research that has been conducted to date on hypervelocity, nearly as many methods for projecting particles have evolved as the number of experiments themselves. The light gas gun and "shaped" charges comprise the vast majority of those methods of projecting particles used to date. Rather than list all the different types of equipment used, we classify them into four basic groups and briefly describe each.

Light Gas Guns

The most common type of light gas gun consists of a breech, a pump piston, a pump tube filled with a low atomic weight gas, and a launch tube extending forward from the pump tube (figure 6). The gun functions by compressing the gas in the pump tube to a very high pressure by driving the pump tube piston down the tube; the piston is actuated by an explosive charge at the breech. A diaphragm placed between the pump tube and the launch tube is then sheared and drives a projectile down the launch tube at a hypervelocity. The upper velocity limit for present light gas guns is approximately 20,000 feet/sec.

Shaped Charges

By properly shaping the explosive charge, the projectile may retain the total energy imparted to it, thereby attaining its highest potential velocity. Figure 7 indicates a basic

idea for the shaped charge. The shapes range from conical and paraboloidal to cylindrical, where portions of the lining of the cylinder are used as the projectiles. This method may be used in conjunction with the light gas gun described earlier. Fogg and Fleischer (23) outline a method of exploding charges sequentially to impart additional velocity to the particle. A projectile passes through the axial hole in the first charge. At a given point, the charge is detonated forming a high velocity jet which boosts the velocity of the particle by ΔV . This process is repeated until the highest attainable gas jet velocity is reached, whereupon the projectile impacts on a target.

Accelerator or Drift Tube Experiments

A potential method for projecting micron diameter metallic particles to hypervelocities creates an electrostatic charge on the particles and accelerates them to high velocities by a machine of either a linear accelerator or an electrostatic type. Hendricks, et al. (24) indicate a method for projecting 0.5 micron (10^{-12} gms of iron or copper) spheres to velocities on the order of 10 km/sec employing a 10 Mev Van de Graff electrostatic generator. There are three attendant problems associated with this method: first, we must accept a multiple particle bombardment of the target; second, the machine used for this purpose must be frequently and thoroughly cleaned because deposition of metallic particles throughout the equipment causes potential shorts; third, we must use metallic particles to eliminate the possibility of simulating the major portion of meteoric materials.

Electrical Discharge

Several workers (14, 25, and 26), in a novel approach to the problem of achieving hypervelocities, employ high energy fast discharge capacitor banks which generate large electric currents for microsecond pulses. Scherrer (25) describes a system employing an expendable barrel type gun. Figure 8 shows a basic setup for this procedure. The capacitor bank is discharged through a fine wire located at the breech of the gun. The wire is vaporized and creates high gas pressures behind the projectile which forces the particle down the barrel at hypervelocities. Scherrer has indicated a potential particle velocity in excess of 15 km/sec. Webb, et al. (26), have been working on a hypervelocity projector of much the same design as Scherrer's except that theirs uses dense agglomerations of materials rather than a single particle to impact on a target. Scully and Cowan (14) generate a high density, high temperature gas by capacitor discharge into a partially confined lithium metal cylinder; the resulting plasma pulls borosilicate spheres down an evacuated tube by aerodynamic drag. These systems are anticipated to achieve, or have been successful in achieving, particle velocities on the order of 10 km/sec or better.

Needs for the Future

Using the foregoing sections and the report of Whipple (27) as a foundation, let us explore some of the directions that future work in hypervelocity should take:

Extension and Correlation of Present Work

Probably the most urgent single objective is the extension of present research to velocities well in excess of 10 km/sec, perhaps to 50 km/sec. Granted, this is no small task especially with the forces imposed on a particle being accelerated to above 10 km/sec in one step. However, these forces can be minimized if the ultimate velocity is achieved in steps using a series of shape charges or a series of capacitor discharges. Velocities must be extended to:

1. Confirm the theory that increases in velocities, decrease the importance of the angle of incidence on crater shape.

2. Prove that scaling laws can be used to predict behavior of particle impact, essentially, to prove that particles with identical kinetic energy, but with differing mass and velocity produce identical effects at speeds above the speed of sound when impacting in the target material.

In view of the fact that no research has been reported using projectile materials of densities or sizes comparable to that of micrometeorites, this is one area which needs exploration. The program may include impact studies of materials having a range in bulk density of 0.05 through 8 gms/cc, and for which kinetic energy is kept constant (assuming scaling laws are valid again).

We have seen that there are many differing theories concerning crater formation, depth of penetration, volume of craters, etc. These theories need to be collected, analyzed and consolidated.

Spallation

At present, there are no data concerning the dynamics of spalled material. There may exist a problem area resulting from spallation in which high kinetic energy material may cause further damage to interior components of a vehicle. Experimentation in this area may include measuring variation of the mass and velocity of spalled material as related to impacting particle kinetic energy, target thickness, and material.

Erosion Effects

Although a small amount of research has been conducted on effects of erosion more work is needed in which fine particles are used at hypervelocities to impact on potential materials for space vehicles.

Satellite-Based Observations

Despite all that may be said in favor of ground-based observations, the fact remains that to study meteoritics properly, observations must be made of the natural particles in the natural environment, i.e., space observations. Although we may not be ready to make full use of the numerous satellites being placed into orbit at present, they may be invaluable in future meteoritic studies. Potential programs include:

1. Mass and Composition of Particles -- Prior to the development of systems to prevent catastrophic puncture of vehicles, it is imperative that a determination of mass and composition of meteoric material be made. This would necessitate catching the particle and recovering the entire system--a task of monumental proportions. The alternate approach would be to combine the "catching" substance or artificial atmosphere with an optical spectrometer to analyze the particle's constituents, thus eliminating the need for recovery.

2. Total Velocity Vectors -- If the velocities of particles, both direction and magnitude, can be determined, then this information combined with the mass distribution will assist in yielding data for the total distribution of matter within at least one astronomical unit of the sun. Whipple (27) lists several potential methods, which can be used with vehicles for obtaining these velocity vectors.

3. Charge on Space Particles -- Determinations of the electrical charge on solid space initiated particles would be useful in studying sun-earth relationships, conditions of the interplanetary gas, and studies of the corpuscular radiation from the sun. Perhaps we could also derive the temperature of the interplanetary gas from measurements of electrical charge on space particles.

In the study of hypervelocity and meteoritics, we have just scratched the surface. There remains a tremendous amount of research to be completed, research that is urgently needed for the proper design both of space vehicles and space experiments. The work yet to be accomplished may also yield answers to questions about motion patterns of particles in space.

I am indebted to Dr. Robert Rolsten of Convair, San Diego, for the sections of his report "Meteor Bumpers" ZS-Mt-014 covering the nature of the environment and analyses of effects of hypervelocity impact, the bulk of which yielded information for the first two sections of this paper.

REFERENCES

1. McKinely, D.W.R., "Meteor Velocities Determined by Radio Observations," *Astro. J.*, 113, 225 (1951).
2. Manning, L.A. and Eshleman, U.R., "Meteor in the Ionosphere," *Proc. IRE*, 47, 186 (1959).
3. Beard, D.B., "Interplanetary Dust Distribution and Erosion Effects," 301, 3*.
4. Broyles, H.A., "Damage to X-ray Detectors by Meteorites," The RAND Corporation Research Memorandum RM-2314 (1959).
5. Beard, D.B., "Meteoric Impact," *ARS Journal* 31, 87, (1961).
6. Kornhauser, M., "Prediction of Cratering by Meteoroid Impacts," *Proc. of the 4th Annual Meeting, Amer. Astron. Soc.* (1958).
7. Partridge, W.S., Vanfleet, H.B. and Whited, C.R., *J. Applied Physics* 29, 1332 (1958).
8. Henderson, R.E. and Stanley, P., "The Effect of Micrometeorites on Reflecting Surfaces," 1960 *Proc. of the Inst. of Environ. Sciences*, April 6-8 Los Angeles, 109-118, (1960).
9. Gehring, J.W., Jr., "Observations of the Phenomena of Hypervelocity Impact," 4, Volume II.
10. Palmer, E.P. et al., *Cratering: Experiment and Theory*, 4, Volume I.
11. Maurer, W.C. and Rinehart, J.S., "Impact Crater Formation in Rock," 4, Volume II.
12. Anderson, G.D., et al., "Cratering by High Velocity Microparticles," 3.

REFERENCES (Cont'd)

13. Gehring, J.W., Jr. and Richards, L.G., "Further Studies of Micro-Particle Cratering in a Variety of Target Materials," 4, Volume III.
14. Scully, C.N. and Cowan, D.L., "Hypervelocity Gun for Micrometeorite Impact Simulation Employing Capacitor Discharge in a Condensed Phase," 4, Volume I.
15. Summers, J.L. and Charters, A.C., "High Speed Impact of Metal Projectiles in Targets of Various Materials," 3.
16. Atkins, W.W., "Penetration Studies," 4, Volume I.
17. James, H.J. and Buchanan, S.S., "Experimental Studies of Penetration by Shaped Charge Jets," 3.
18. Kornhauser, M., "Surface Roughness Caused by Meteoroid Impacts," 3.
19. Beard, D.B., "Interplanetary Dust Distribution and Erosion Effects," 3.
20. Maiden, C.J., Charest, J. and Tardiff, H.P., "An Investigation of Spalling and Crater Formation by Hyper Velocity Projectiles," 4, Volume III.
21. Culp, F.L., "Volume-Energy Relation for Crater Formed by High Velocity Projectiles," 3.
22. Bryan, G.M., "A Model of Oblique Impact," 4, Volume III.
23. Fogg, F.E. and Fleischer, C.W., "Acceleration of Projectiles with the Sequenced High Explosive Impulse Launcher," 4, Volume I.
24. Hendricks, C.D., Shelton, H. and Wuerker, R.F., "Electrostatic Accelerator for Impact Studies," 3.
25. Scherrer, V.E. and Richards, P.I., "An Exploding Wire Hypervelocity Projector," 4, Volume I.
26. Webb, F.H., et al., "Massive Hypervelocity Particles by Electrical Means," Electro-Optical Systems Inc. Report No. 470-2Q-2 (1960).
27. Whipple, F.W., "Solid Matter in Space," J. of Geophysical Research, Nov. (1959).

* 3 refers to the proceedings of the Third Symposium on Hypervelocity Impact, Armour Research Foundation of Illinois Institute of Technology, Chicago, Illinois (1958).

4 refers to the Fourth Symposium on Hypervelocity Impact, APGC-TR-60-39 (Volumes I, II or III) September 1960.

DISTRIBUTION of VELOCITIES for SOME 11000 METEORS

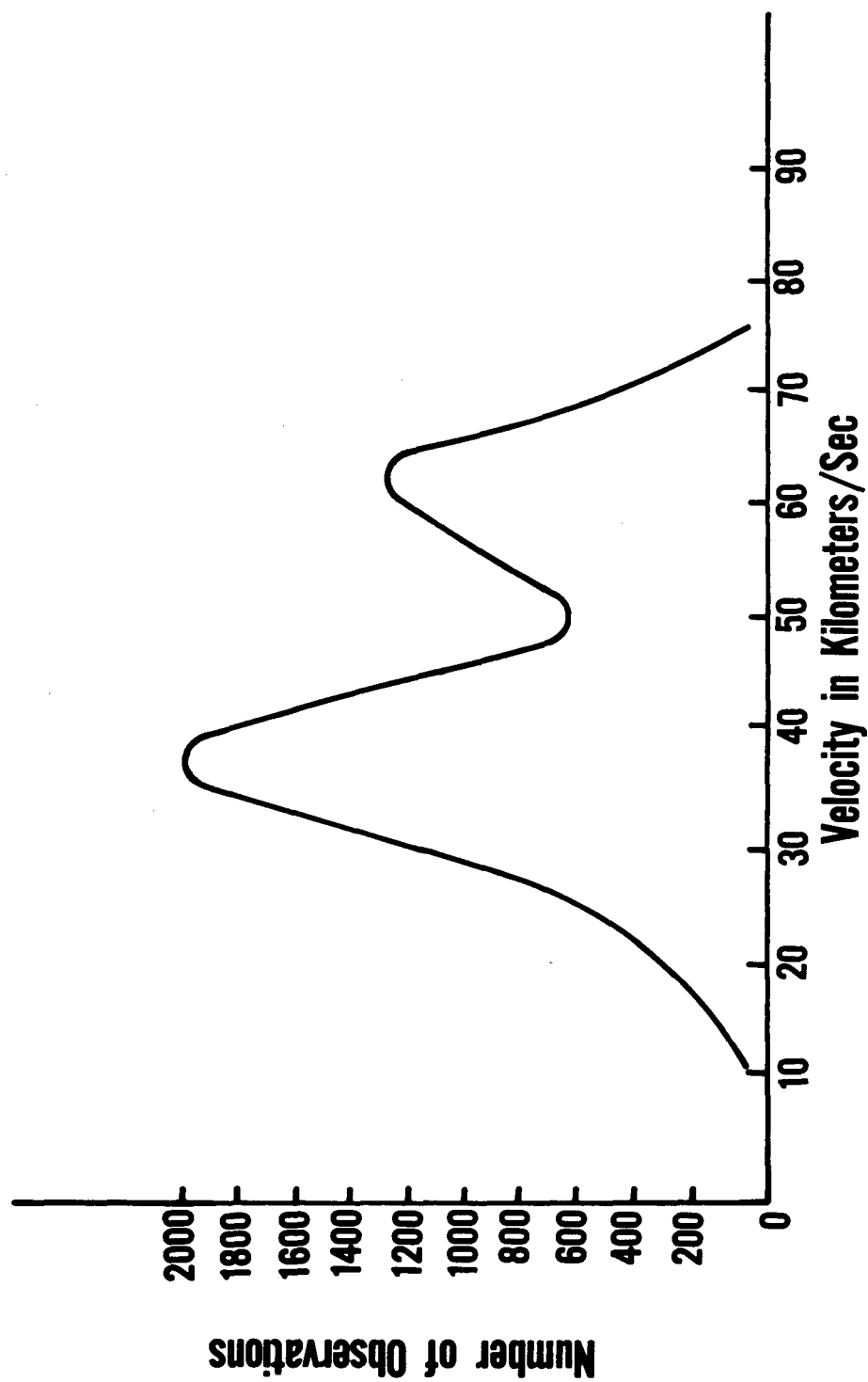


Figure 1.

METEORIC FLUX vs MASS

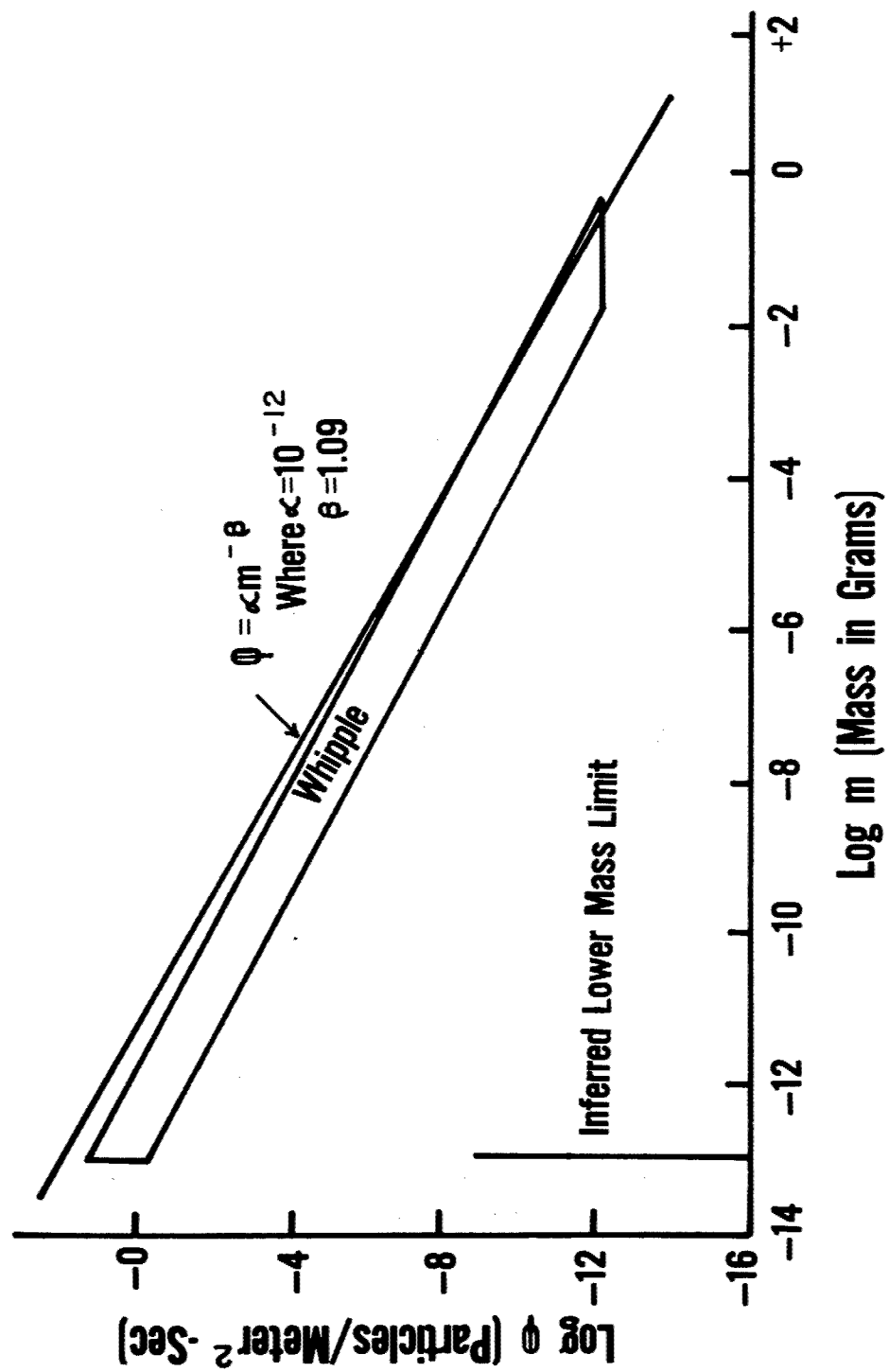


Figure 2.

VOLUME/UNIT KINETIC ENERGY VS PARAMETER $\frac{1}{C^2 \rho}$

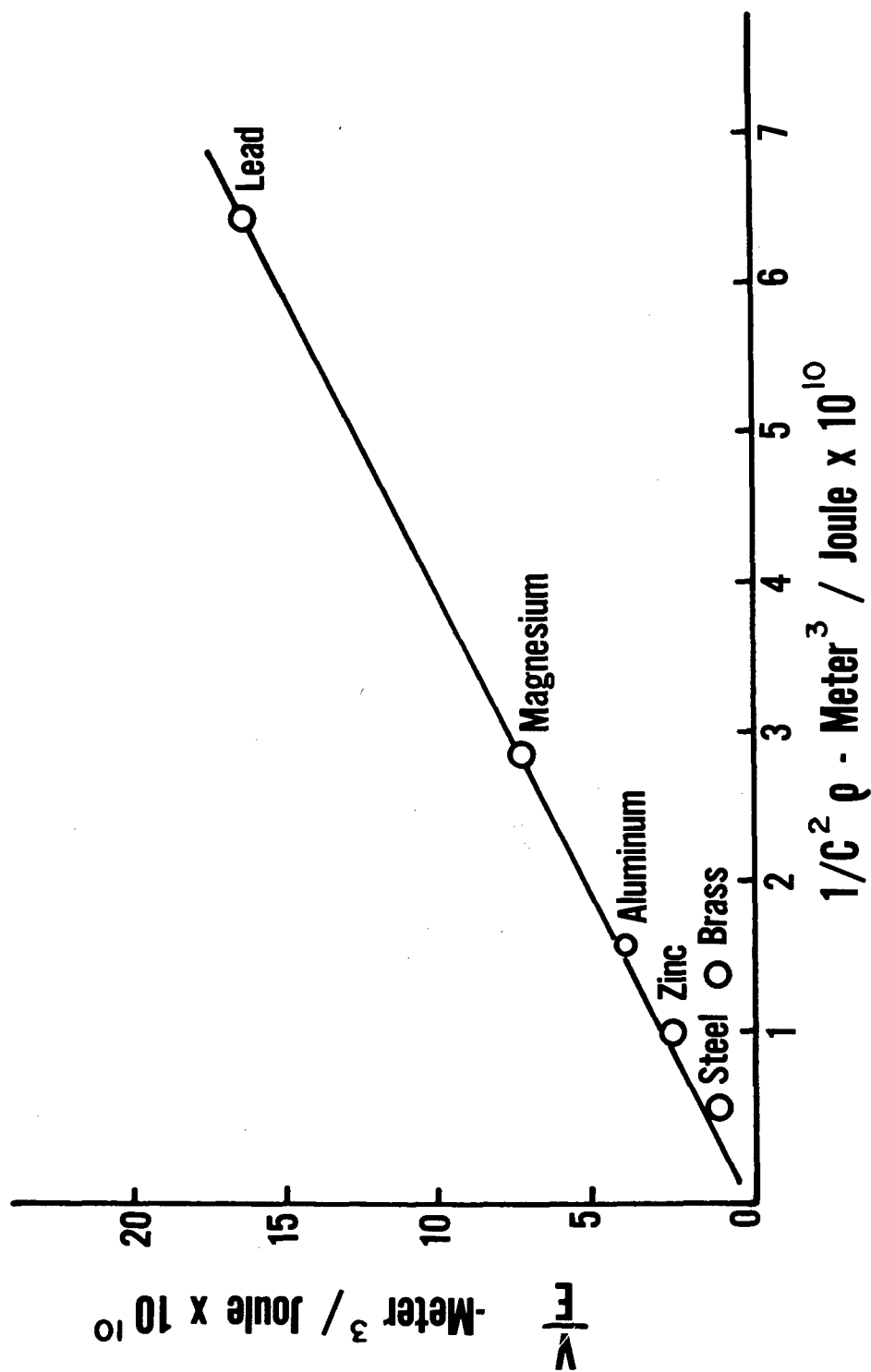


Figure 3.

CROSS SECTION of METEROID IMPACT

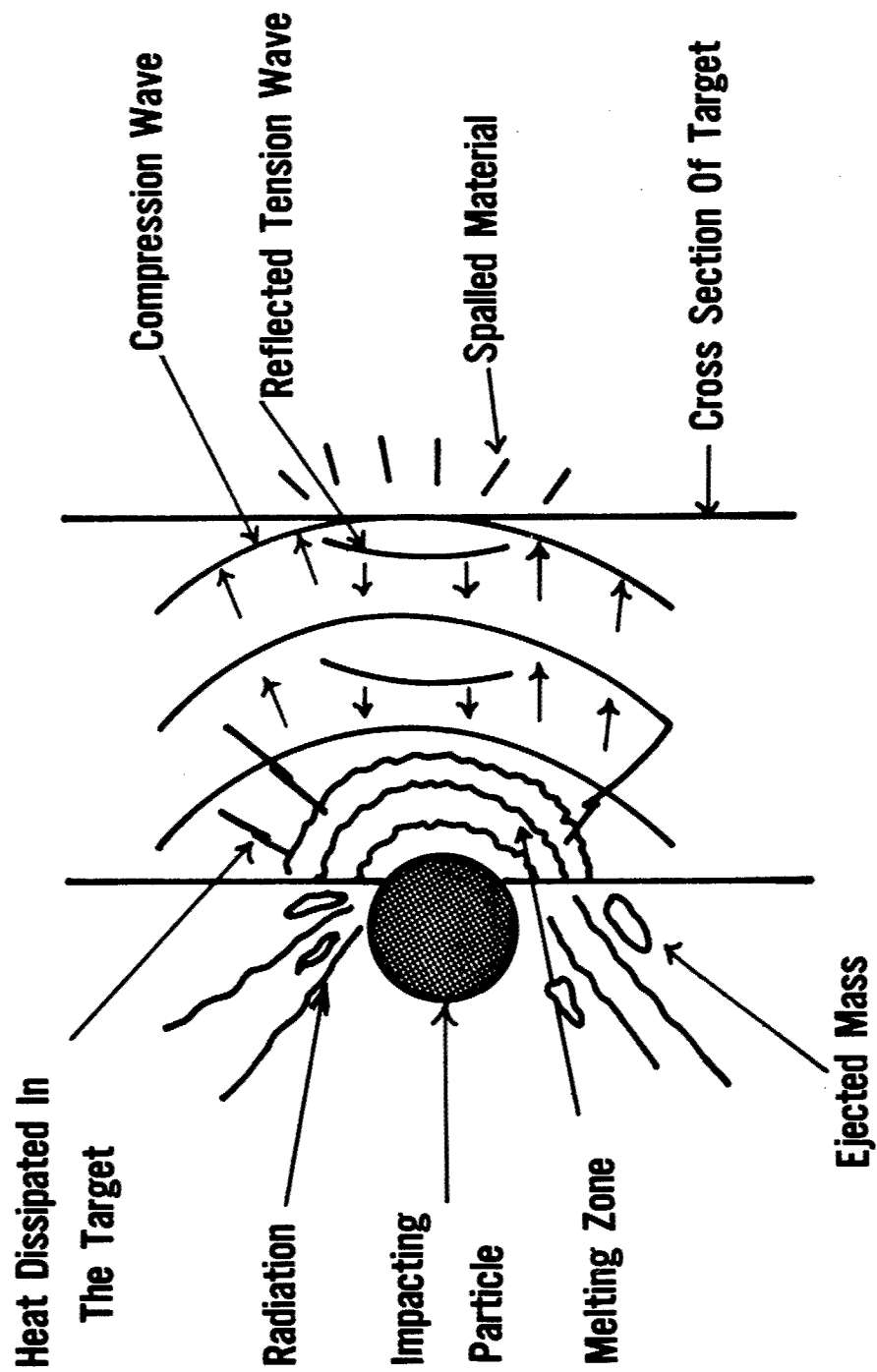


Figure 4.

CRATER SHAPE vs ANGLE of IMPACT

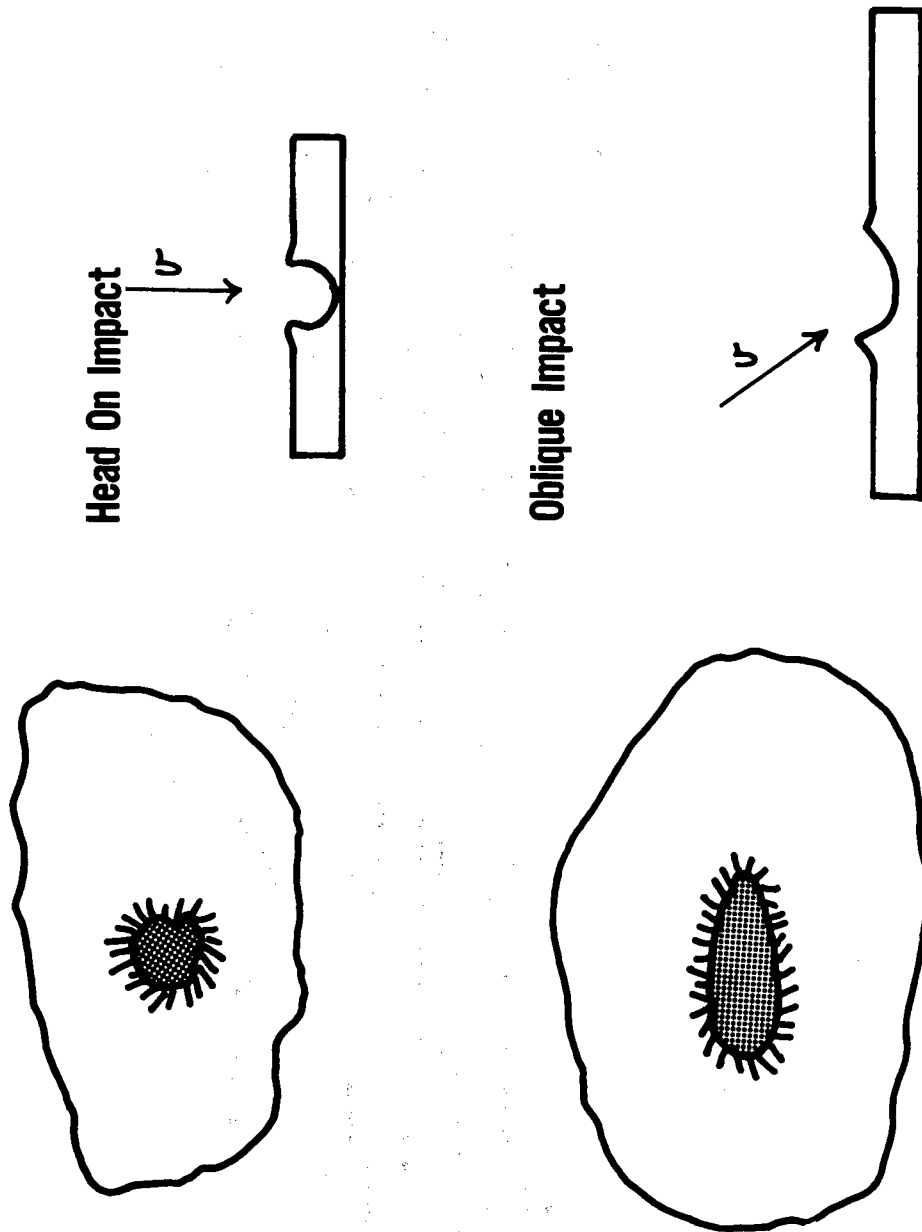


Figure 5.

BASIC LIGHT GAS GUN

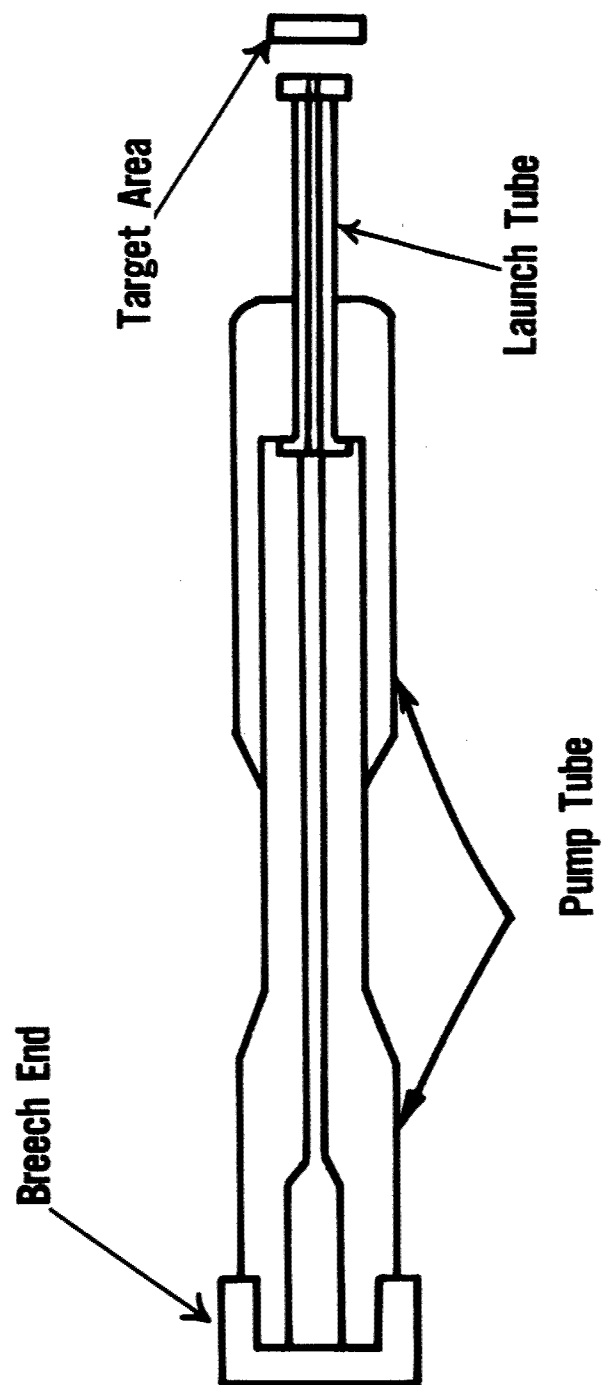
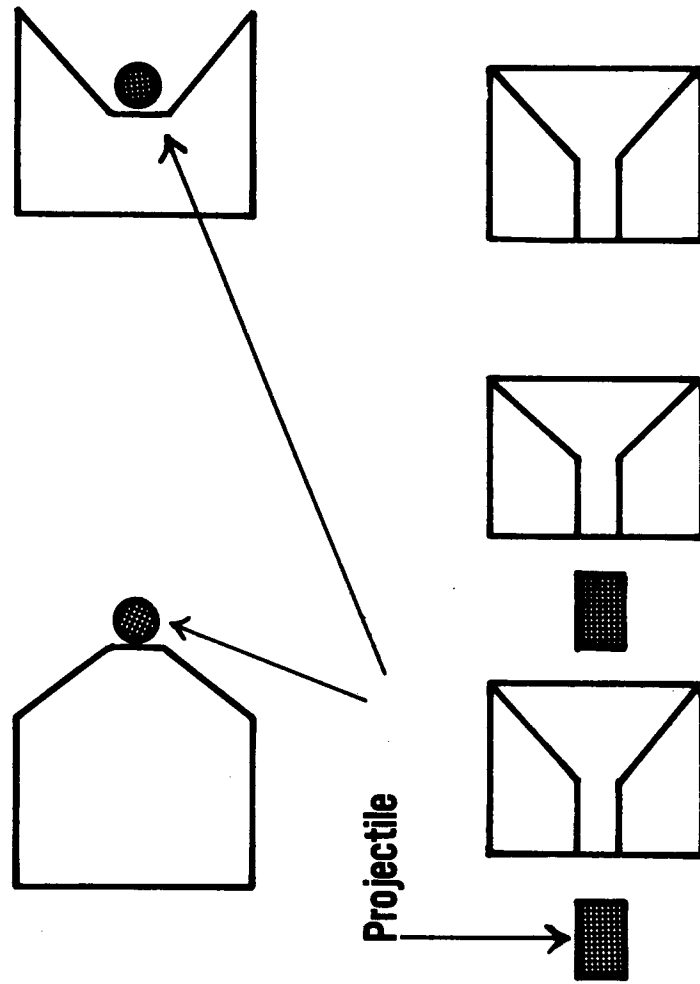


Figure 6.

TWO BASIC SHAPE CHARGES



POSSIBLE SEQUENTIAL VELOCITY BOOSTER

Figure 7.

CAPACITOR DISCHARGE PROJECTOR

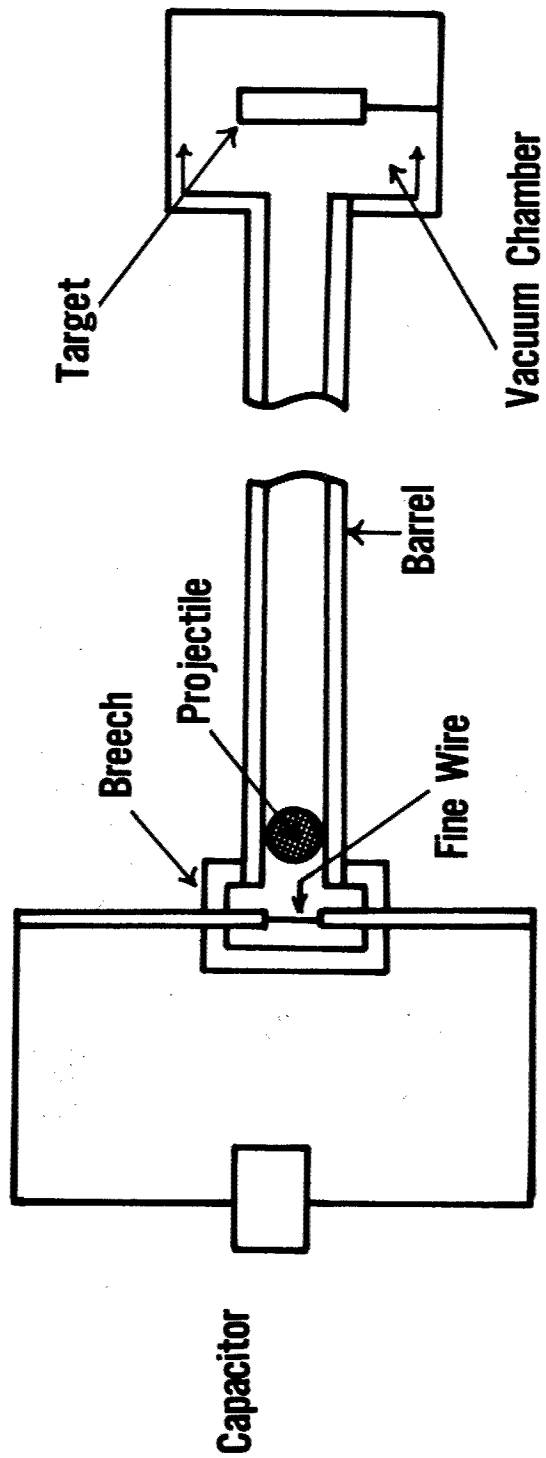


Figure 8.

MATERIAL INFORMATION AND DESIGN DATA

Chairman and
Speaker

Mr. D. Shinn

Panel Members

Mr. J. Wittebort

Mr. E. Dugger

MATERIALS INFORMATION AND DESIGN DATA

D. Shinn

Directorate of Materials and Processes, ASD

The development of materials property design data for aerospace applications has been in process ever since Orville Wright flew the first airplane. Despite this mass of data which has been developed over nearly sixty years, ever-changing technologies require an accelerated effort for generation of materials property information of sufficient quality and quantity for design support purposes on a timely basis.

The Directorate of Materials and Processes, ASD, placed emphasis on filling the more critical gaps in specific materials information areas since it cannot hope to produce all desired data. Three types of gaps seem to stand out insofar as data generation is concerned, namely: (1) Information on promising newly developed materials or material systems is not available, (2) Available information on established materials is of questionable quality or testing conditions, and (3) Available information on existing materials is based on too few tests and too few lots of the material.

Each of the above points warrants a bit of additional discussion. For example, in considering the first gap in view of continuous and rapid development of new materials, we wonder, "How early in the development in a given material should the generation of design data begin?" It is, of course, customary to screen data concurrently with development effort. However, before a design engineer can incorporate a new material into a final design, it is necessary to have comprehensive and reliable materials property data. In the past, the design engineer was satisfied with mechanical property data, but now additional properties such as the thermophysical and electrical properties of materials are necessary to make more efficient design usage.

The second gap concerns the inadequacy or questionable quality of existing and available information on established materials. This deficiency has been most pronounced in the area of thermophysical properties, although it applies in part to mechanical properties as well. Because of the lack of standardization of measurement techniques, problems concerning thermophysical properties, published in great volume in the literature, are still not fully resolved. These include thermoconductivity of metals and nonmetallic materials, of sandwich and composites, and emissivity. In the area of mechanical properties we face such criteria as notch sensitivity; thermal shock; low cycle fatigue; and time, load, and temperature simulation requirements. Although there is concerted effort on the part of industry to resolve this problem, there is still much to be desired. More sophisticated types of materials evaluation require more information on the effects of load-time-temperature environment on various types of materials and their properties. This would include structural plastics, ceramics and intermetallics, composites, refractory metals and their coatings, insulating materials and materials systems.

Air Force objectives strive to:

- (1) Provide in-house facilities and techniques to obtain engineering data on promising newly developed materials with a minimum of delay.
- (2) Determine from such engineering data whether it is feasible to obtain more comprehensive design data on the new materials, and

(3) Appraise the necessity for more specialized tests, such as effects of load and temperature spectra and the effects of environment, to bring out unique advantages or limitations in the applications of the new material.

The extent to which all of the above shall be conducted must be evaluated since use of the material is also dependent on such factors as producibility, fabricability, and the availability of uniform material in commercial quantities.

To help achieve these objectives and to overcome some of the obstacles prevalent in design because of insufficient data, a number of programs are being conducted by the Air Force which will provide the necessary equipment for accurately obtaining the data needed. Predominant are means for high temperature data generation which involves both development of better heating facilities and property measuring techniques at these high temperatures. One significant example of the type of progress needed in many areas is shown by the successful development in this area of direct strain measurement over a 2-in. gage length of tungsten up to 4750°F. The resultant curve is shown in figure 1. To the best of our knowledge there has been no other such strain recording at this temperature; yet, a much broader capability in this area is needed.

One aspect of this improvement is the development of new methods for presenting design data. As with most novel approaches, the reception of these procedures has been slow, but just as the Ramberg-Osgood parameters, and then the Larsen-Miller parameters were utilized for data interpretation and prediction, so is it expected that the test of time and use will more fully develop other methods which can be universally accepted.

One of the more recently proposed methods, which is particularly connected with prediction of results, is a means of determining the strength of a material after it has been subjected to various temperature and time histories. An example of this shown in figure 2. Another involves creep data prediction by use of a nomograph in which the amount of creep strain in a given material can be determined if the stress and time are known (figure 3). Still a third relates creep and fatigue data and the limitations that creep superimposes on fatigue (figure 4). Another provides a statistical means of determining the extent of tests to be accomplished for obtaining valid data as indicated in figure 5. These methods are still in the early stages of evaluation but are representative of the type of thought being given to presenting data in meaningful ways.

The third type of gap, involving too few tests and too few lots of material on which property information is furnished, ties in directly with the data collection problem. Although tests conducted by one organization may be insufficient adequately to authenticate its data, data from other sources may support or negate the results if test information were only made available through publication in the literature.

This third gap logically brings us to one of the basic difficulties with materials research in particular and scientific research in general, namely, lack of transmission of information and data.

The generation of data is naturally of very little value other than to the originator if the results are not distributed to other scientists or engineers. One of the basic problems, however, is to get these results to the people who could properly use them. Possibly, all have had the experience of the very great problem of attempting to read everything available in a field of interest. In many cases, the very piece of literature needed to solve a specific problem under consideration goes unread, undigested, and unused. This is due

in part to the extensive boom in scientific and engineering literature in the past several years. It has been estimated that in every 24 hours, enough technical papers are prepared to fill seven sets of a 24-volume Encyclopedia Britannica. This represents approximately 60 million pages of scientific literature per year. It has also been estimated that research and development comprises 2 1/2 percent of our gross national product. Again, it has been estimated that the present cost to the United States in documentation, storage, and retrieval of information alone, is approximately one billion dollars. Nevertheless, basically, the result of research and development is information which must be transmitted before it is truly effective. It is significant that up to 50 percent of our research and development effort is wasted because of poor information exchange. These facts indicate how extremely difficult it is for a laboratory scientist or engineer to stay abreast of his field. He must be aided, therefore, in receiving information pertinent to his field by having as much as possible of the extraneous matter and information removed.

Information agencies established during the past few years have begun to fill this particular need in the scientific community. (They also play an important role in actual laboratory scientific research.)

Concurrently, materials research, too, has increased at a rapid rate over the last several years. As in many other fields, advanced technical requirements have dictated the development of new materials or the adoption or restudy of old materials with new requirements in mind. There has resulted, therefore, in many articles, reports, and books detailing the role of various materials in these new technologies. It would be difficult to estimate how many. But, as an example, the Directorate of Materials and Processes alone has generated in 20 years over 10,000 reports of various types pertinent to the Aerospace Materials Industry. Add to this similar efforts of other Government agencies and private industries studying aerospace materials and it can be easily estimated that over 1/2 million reports in this category have been developed, representing a wealth of information. Unfortunately, some of these reports receive limited distribution, others obtain scant attention when received because of other pressures on potential readers.

The Directorate of Materials and Processes has attempted to correct this situation. It has circulated over 3/4 million copies of its reports in an effort to keep the Aerospace Materials Industry informed. It has recognized the fact that to establish the most fruitful materials research programs, its own scientists and contractors must have available to them the most recent information on what has been and what is being accomplished in their particular field. Additionally, a comprehensive program has been established concerned with efficient collection, judicious evaluation, and systematic storage of data. Obviously, this program is a tremendous help in relieving the "materials" man from many hours of "digging for data" and frees him to exert his efforts on more rewarding tasks.

While every aspect of information or data processing is important, the first step, naturally, is the collection of data. This is being accomplished in several ways as follows. The Directorate

- (1) Obtains copies of all reports prepared by the Directorate of Materials and Processes and its contractors.

- (2) Screens all reports issued by the Air Force Systems Command and utilizes those which have reference to materials.

(3) Receives information of current materials research programs being conducted by the Army, Navy, and the Air Force, both under contractual effort and internal research.

(4) Collects all reports through the DOD Departmental Agencies or ASTIA pertinent to materials.

(5) Negotiates agreements with Weapons Systems or Aerospace contractors to obtain materials data from their records which may not have been previously published because of lack of time or money. (In this effort we are receiving data on over 125 materials.)

(6) Obtains data or information as a result of screened abstracts in the materials area.

Evaluating properly and correlating data is of paramount importance to its use. Reliability in this effort can only be ascertained by people who are knowledgeable in the particular materials discipline which is being considered. As part of our collection program, we require that whenever possible we obtain all the information pertinent to the results that have been obtained such as the heat treating process, test techniques used, the specimen geometry, the strain rate, the environmental conditions involved; in short, as much information as can possibly have any effect whatsoever on the overall results. These factors are, of course, carefully considered during data evaluation in determining its overall reliability.

Information or data storage must of necessity be tied in with the method of retrieval since a competent storage and retrieval system is the crux of the advantage of data or information to the scientific user. If it isn't in the system, or if it cannot be located even if it is in the system, it is, of no value to the investigator. Systems for storing materials information are many. The Directorate has adopted a coordinate indexing system, at present on a manual basis, with the expectation that a machine method will be adopted later.

Adequate dissemination of data is, of course, the most important part of the overall program. Several methods are being used and include:

(1) Processing specific requests for information or data.

(2) Preparation and distribution of data sheets and state of the art reports on pertinent materials.

(3) Publication of digests on current materials programs.

(4) Routine distribution of specific available information to known users of such data.

Specific programs in effect in the information processing activity fall presently into three categories, namely, processing of information, data sheets, and handbooks. Coincident with the information processing system, studies are made of the basic requirements in information processing systems and an examination of existing information centers, the type of information handled, the manner in which it is being processed, and the problems involved to identify areas where there is a lack of effort or data, to devise and implement an awareness program among potential users of materials data, and to develop a limited central literature searching activity.

Back of processing materials knowledge is the philosophy that specialized information can best be handled by organizations that have a good deal of background in a particular materials area. The Directorate has concentrated in the past year on three specific areas so far as establishing information programs are concerned. These are: First, activities in which thermophysical properties are the prime product; second, electronic and electrical properties; and third, mechanical properties. Many have heard of and know quite well the Thermophysical Properties Research Center (now about four years old) located at Purdue University. The Directorate partly sponsors this activity and supports programs to obtain data on thermoconductivity of ferrous and nonferrous alloys and 28 gases; emissivity of pure metals, alloys, and coatings; specific heat of pure metals and alloys; and viscosity of 28 gases; plus support of volume II of the Retrieval Guide. Those who have had the opportunity to review the volume I of Retrieval Guide know its immense potentialities and its significant advances in the field of thermophysical properties of materials. The second program, Electronics and Electrical Properties Information, has as its purpose to collect and publish data sheets on properties of materials which could be used for electronic or electrical applications. This effort has just come into being and the first part of the program is concerned primarily with establishing the system to be utilized and with performing the initial work on semi-conductors. The Mechanical Property Information effort has not yet reached the stage of completion which the other two activities have. However, during the past year, much of the work that would normally be accomplished in processing data sheets on mechanical properties has been accomplished through contracts in other areas. Currently, a great deal of fatigue data and creep data have been obtained, and other types of materials properties to a somewhat lesser degree. All of which are being processed and distributed to Aerospace Industries as required.

Establishing other information programs for specific types of properties or materials has been considered but additional guidance is needed from the Aerospace Industry.

Adequate service in these information programs requires working closely with established materials information centers such as the DOD sponsored Defense Metals Information Center (DMIC) at Battelle and the Plastics Technical Evaluation Center at Picatinny Arsenal. This association includes mutual exchange of information and coordination of programs. In the case of DMIC, the Directorate has been assigned contract monitoring responsibility. There are, of course, many other information activities, both government sponsored and private. A report listing those concerned with materials has been prepared so that their services may be used whenever needed.

Handbooks have always been, and probably will continue to be, used to a great extent by the practicing engineer for basic and empirical information. In the design of components, handbooks give, most readily, information which can be transmitted to the drawing board. It is imperative, as it is in such information, that the contents of the handbook be pertinent, accurate, and of the type that will be of the most use or will lead to the most useful information in the specific area. Some of the handbooks of particular concern are:

(1) A design Handbook on Structural Plastic Materials. This handbook will include properties of structural plastic materials, design criteria, stress analysis for specific applications, processing and tooling information, and its effects on properties, testing, and quality control.

(2) A Handbook on Properties of Metals and Alloys. This handbook is a continuing effort which resulted in the Air Weapons Materials Application Handbook, Metals and Alloys. This publication contains a comprehensive listing of a number of metals covering

all aspects of information and properties on a large number of metals. The continuation effort includes 40 metals and alloys not listed in the current handbook and includes titanium, aluminum, low alloy and carbon steels, martensitic and austenitic stainless steels, ultra high strength steels, cobalt and nickel based alloys and refractory metals. As indicated earlier, the various types of properties, whether normally considered design data properties or not, are included.

(3) Electronic Encapsulating Materials Handbook. This includes information on potting and encapsulating materials for insulation, shock protection, and moisture proofing of electronic equipment and components. This handbook is now in the process of being printed and will contain approximately 500 pages of properties and materials covering epoxies, polyesters, urethanes, silicone rubbers and thermoplastics. Information is also given on applicable temperature ranges of these materials.

(4) Handbook on Elastomer Design. This includes information on elastomer properties, design criteria and methods in application information on a wide variety of elastomer materials. It is designed to assist the component designer in elastomer selection.

(5) MIL-Handbook 5, Strength--Metal Elements; MIL-Handbook 17, Plastics for Flight Vehicles; and MIL-Handbook 23, Composite Construction for Flight Vehicles. These handbooks are supporting the design books containing data which have been verified as to their practicability and usefulness for design. (The Navy and FAA assist in their preparation.)

As part of the program, MIL-Handbook 5 is being placed on magnetic tape which will contain all of the data now in the handbook. This is a pilot program to determine the feasibility of putting all similar handbooks on magnetic tape for easy and versatile retrieval.

In summary, then, we would like to emphasize five points which we think are necessary to ensure the proper selection of materials to be used in design. These are:

(1) Continued effort to develop improved criteria for evaluation of materials which more closely relates them to conditions anticipated in service.

(2) Development of commercially available testing equipment for

(a) Simulation of load-temperature-environment based on service conditions, known, and projected.

(b) Determination of thermophysical properties within the present state of the art, i.e., thermal conductivity, and emissivity (total normal, spectral, and total hemispherical).

(3) Freer exchange of conventional data obtained by industrial organizations on like materials to enhance the objectivity of property appraisal and to add to the reliability of resulting property values.

(4) Broader use by industry of similar techniques, equipment, and criteria to obtain the same properties on the same classification of materials.

(5) More detailed description of equipment and techniques used for generation of property data.

BIBLIOGRAPHY

1. "Design Data Manual for Tungsten," Letter Report, 15 April 1961. Hughes Tool Co., Contract AF 33(616)-7385.
2. "Format Proposed for the Presentation of Fatigue Data", Report No. SM-23836, 12 February 1960. Douglas Aircraft Co.
3. "Analysis of Creep Data for Metals" - Letter Report, 10 April 1961. Boeing Airplane Co., Contract No. AF 33(616)-7201.
4. "Design Strength Data for Severe and Complex Thermal Environments," C.D. Brownfield, Northrop Corporation.
5. "Coordination of Information on Current Scientific Research and Development Supported by the United States Government," 17 April 1961. U.S. Government Printing Office.
6. "Bibliography of the Mechanization of Information Retrieval," February 1961, Stanford Research Institute.
7. Shera, J.H., Kent, A., and Perry, J.W., Information Systems in Documentation, Vol II, 1957.
8. "Current Research and Development in Scientific Documentation No. 7," Nov 60, National Science Foundation.
9. "Nonconventional Technical Information Systems in Current Use," March 1960. National Science Foundation.

STRESS-STRAIN CURVE FOR TUNGSTEN

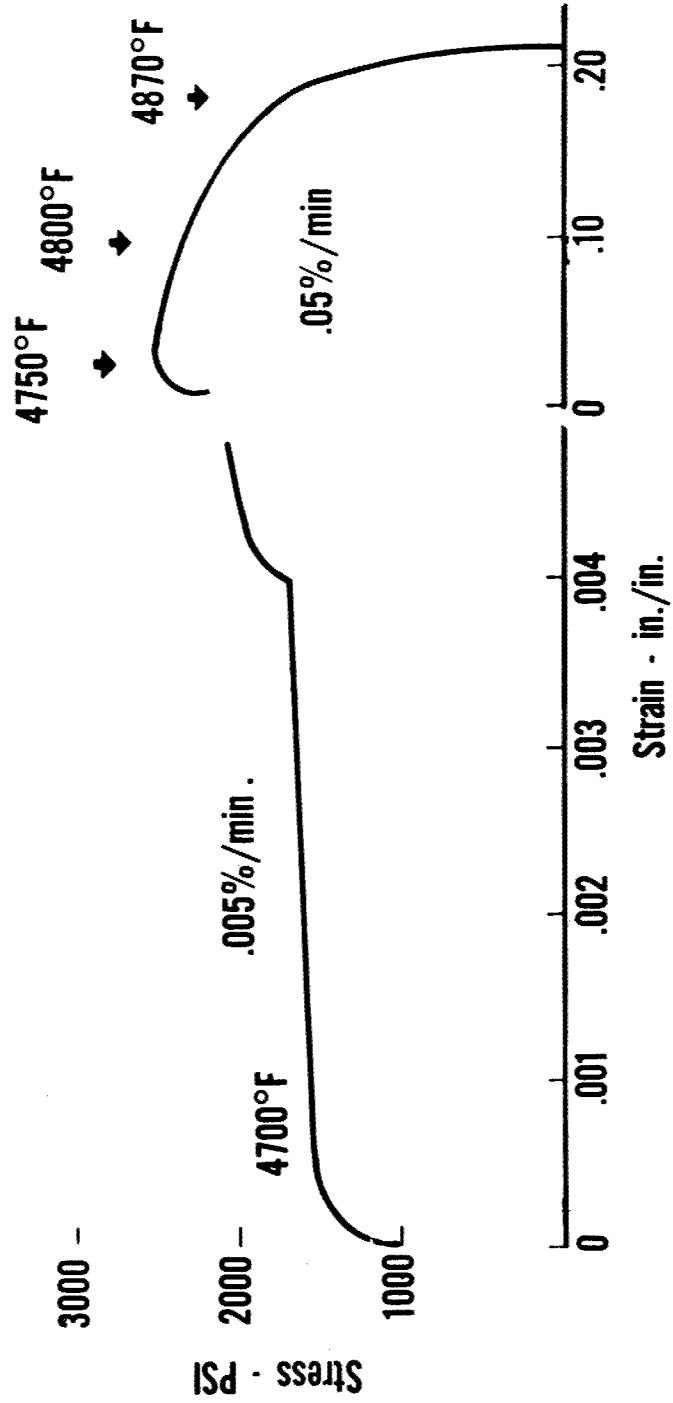


Figure 1. Stress-Strain Curve for Tungsten

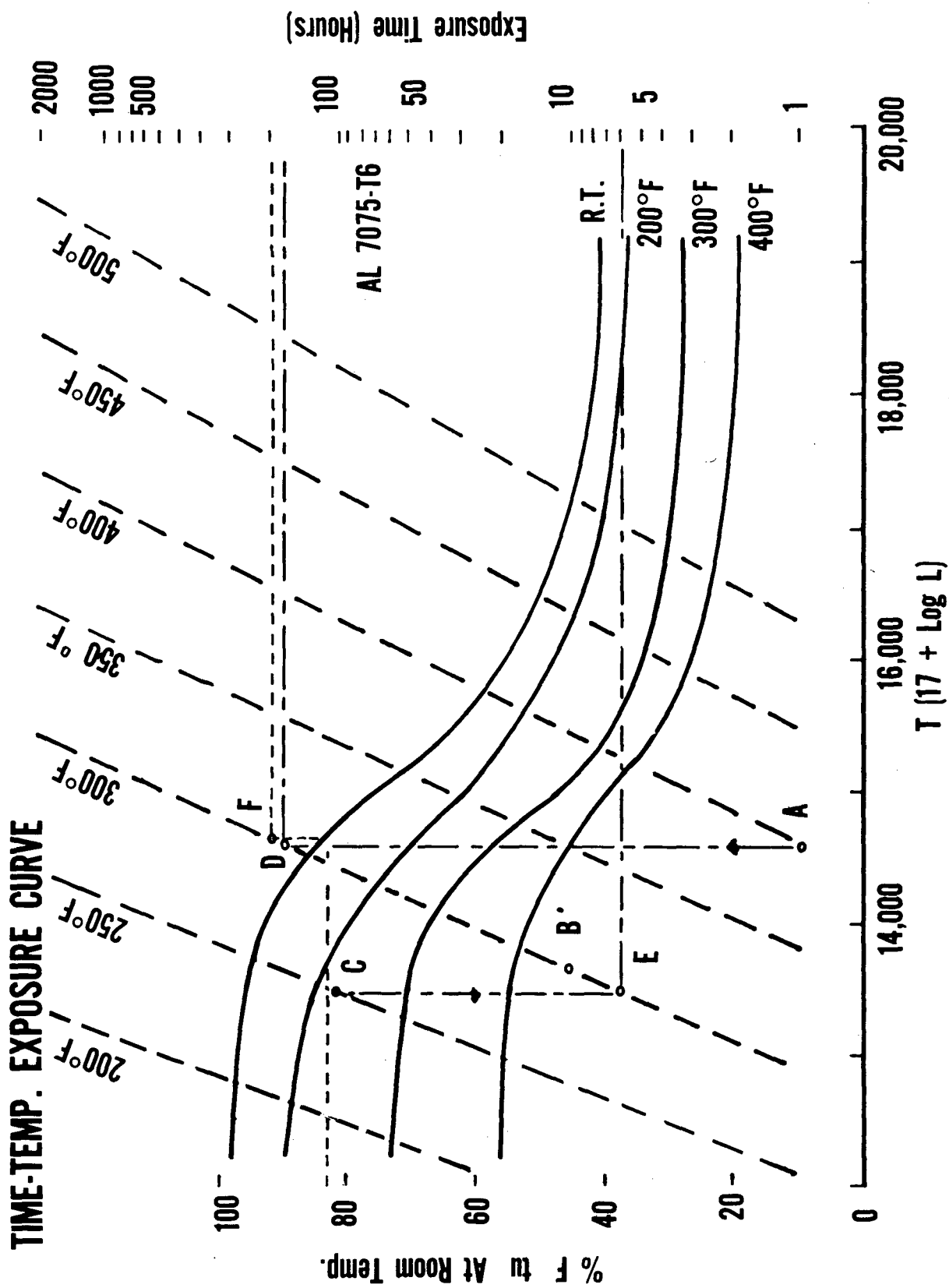


Figure 2. Time-Temperature Relationship

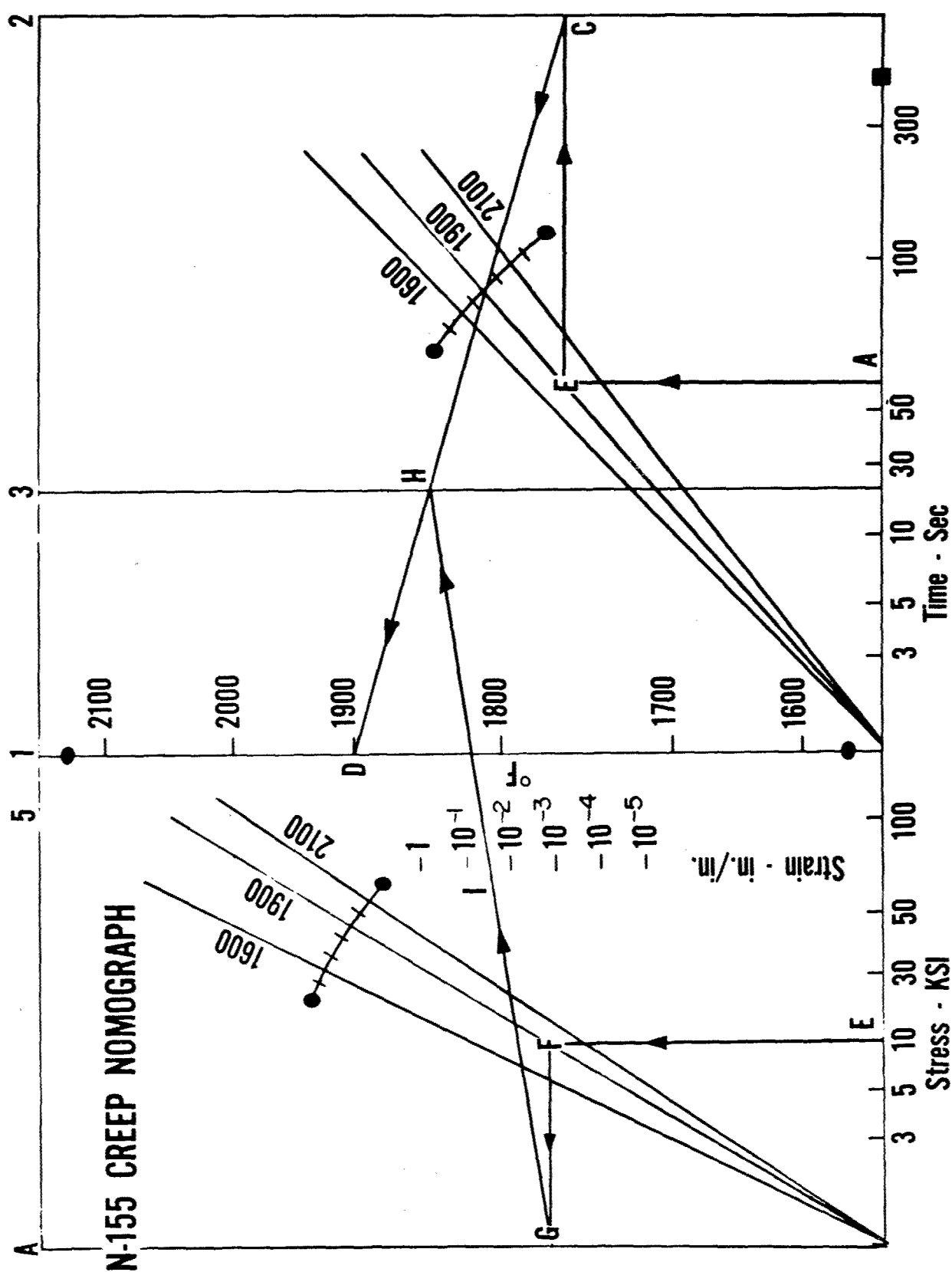


Figure 3. N-155 Creep Nomograph

FATIGUE DIAGRAM

S - 816 At 75°F
F = 3600 Cycles/Min
Ref: WADC TR 56-181
Unnotched Specimens

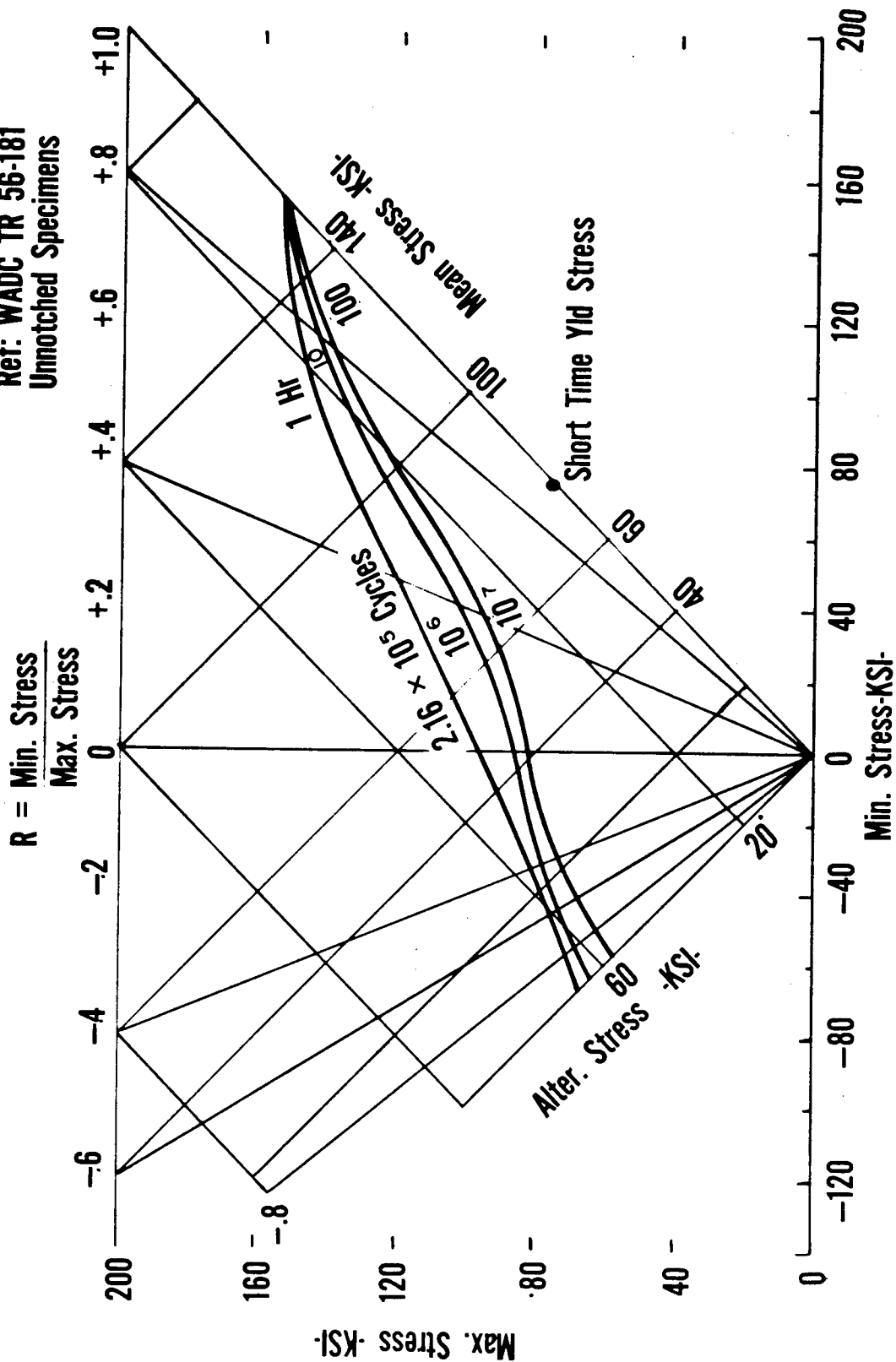


Figure 4. Fatigue and Creep 24S-T4 500°F Data from WADC TR 53-510 I

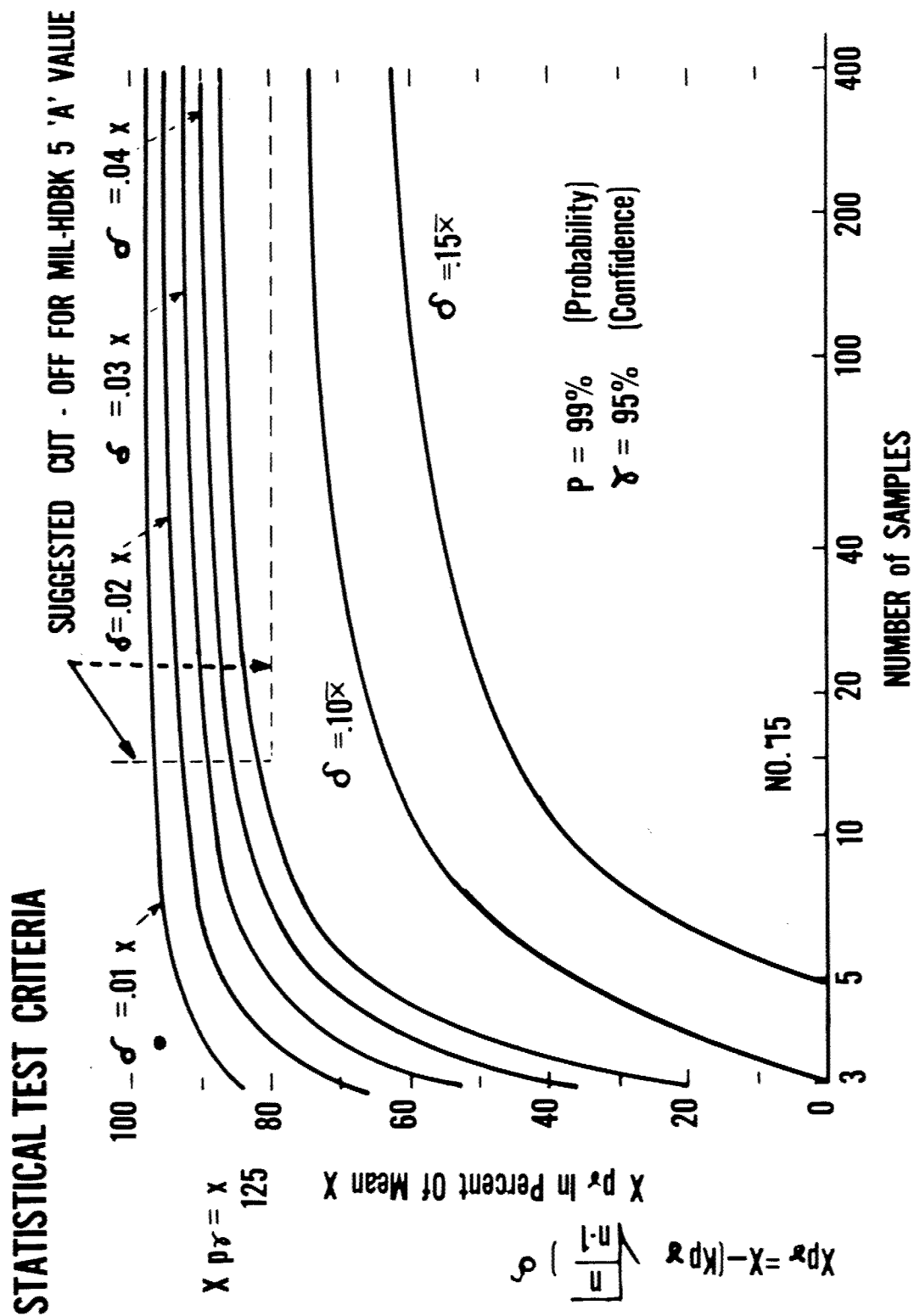


Figure 5. Statistical Test Criteria

ANALYTICAL TECHNIQUES

Chairman

Capt. S. Brokeshoulder

Speakers and

Mr. H.M. Rosenberg

Panel Members

Mr. W.L. Baun

Dr. L.A. Harrah

Miss M.T. Ryan

Mr. F.F. Bentley

ELEMENTAL MICRO ANALYSIS

H. M. Rosenberg

Directorate of Materials and Processes, ASD

Elemental organic analysis is that area of chemistry that is concerned with the quantitative determination of the elements in organic compounds. The micro analyst utilizes samples weighing less than 5 milligrams.

Elemental organic analysis plays a central role in support of organic chemical research. It provides the data necessary to determine the structure of a new compound. The Air Force is engaged in the study of compounds which have potential applications in the formulation of polymers and synthetic lubricants. The products generated by these studies seldom exceed 100 milligrams and without the techniques of microchemistry these programs would not be feasible. Micro techniques have the additional advantage of being more rapid than corresponding macro procedures and are used even when large samples are available.

Micro analysis had its inception 50 years ago. The invention of the micro balance, at that time, enabled Pregl to develop the techniques for which he won the Nobel Prize. Many of his methods are still in current use. Figure 1 shows the Ainsworth micro-balance, which can weigh a 20 gram load with a precision of .002 milligrams.

In general, an analysis consists of the destruction of the molecule, followed by the separation and measurement of the elements. There are approximately 1,000,000 known organic compounds with great differences in composition, structure, and properties. Since the analytical approach must be predicated on composition and properties, a wide variety of techniques are required. It must be emphasized that no single procedure is universally applicable for a given element on all compounds. Methods must often be custom-made to do a given job.

A description of some representative techniques are given below. Figure 2 illustrates a carbon-hydrogen analyzer. A weighed sample is heated in a platinum boat in a regulated atmosphere of oxygen. The combustion products are swept through a combustion tube which contains reagents for insuring completeness of oxidation and removal of extraneous elements. The water and carbon dioxide are selectively absorbed and determined from the gain in weight of the absorption tubes.

The effectiveness of many different reagents have been studied and there is no general agreement regarding the best method for packing combustion tubes. A rapid combustion method has been developed in which the compound is oxidized in a rapid oxygen stream in an empty combustion tube (1). This method has not gained favor in this country but seems to be in extensive use overseas.

Figure 3 shows a Dumas nitrogen apparatus. The sample is oxidized by copper oxide and the liberated nitrogen is swept into a graduated vessel by a stream of carbon dioxide. The carbon dioxide is absorbed in a strong alkali solution and the volume of nitrogen is measured. (An automatic apparatus is on the market which is claimed to be capable of performing an analysis in less than ten minutes.)

Figure 4 illustrates a Shoniger flask. It is a simple device in which a weighed sample, held in a platinum basket, is combusted in an atmosphere of oxygen. It has proved effective

for the decomposition of a great variety of compounds and is rapidly replacing the use of sealed glass and metal bombs. This technique, on a micro scale, was introduced in 1955 and is used in the determination of halogens, sulfur, and phosphorus (2). Additional adaptations and refinements of this technique are appearing regularly in the literature. For comprehensive treatment of organic micro analysis the reader is referred to references 3, 4 and 5.

The synthesis of new compounds requires the concomitant development of analytical methods. The analysis is often more difficult than the preparation of the compound. Many compounds that are being studied by the Air Force pose challenging problems since they are frequently designed for a high degree of thermal and chemical stability and incorporate the use of unconventional elements in unusual combinations. Micro chemists often dream of an instrument which will provide a rapid and accurate analysis for all elements simultaneously, with a minimum of manipulation.

In recent years a new dimension has been added to analytical chemistry which offers a promise for the fulfillment of this dream. Various radiation sources have been applied successfully in the area of elemental analysis. The use of X-rays, beta-rays and neutrons appear most promising (6).

X-ray methods are analogous to other electromagnetic radiation methods such as infrared, visible, and ultra-violet. The X-ray absorption method relates the concentration of elements to the amount of absorbed radiation at specific wave lengths. Radio-active isotopes are sometimes used as the X-ray source. For example, several laboratories are using iron-55 for the determination of sulphur, chlorine, and bromide in organic compounds.

X-ray fluorescence methods measure the amount of X-rays emitted after excitation. Figure 5 is a schematic of the operating principle behind this method. The sample is excited by an X-ray beam. The resultant fluorescent radiation is collimated and its wave lengths are separated by a crystal which acts as a diffraction grating. The analyzing crystal is slowly rotated and the intensity of the X-ray spectrum is measured with a Geiger counter. This method is being used for the determination of iron in hemoglobin, sulphur in oil, and lead in gasoline.

Since the lighter elements do not emit or absorb X-rays in the regions normally used, other radiation must be employed. Beta-ray and neutrons have been used in the determination of hydrogen. Beta-rays are most strongly absorbed by the light elements particularly hydrogen. Under controlled conditions, hydrogen concentration can be determined by means of Beta-ray absorption. Commercial equipment is available which uses strontium-60 for its Beta-ray source. Neutron activation analysis can be used for selected elements in organic materials and neutron moderation or slowing-down can be used as a measure of hydrogen concentration (see figure 6).

This brief discussion of radiation analysis is by no means comprehensive. It is intended to indicate a rapidly growing area which may displace many classical methods in the near future.

REFERENCES

1. Belcher and Ingram, Anal Chem Acta, 1950, 4, 118.
2. Schoniger W., Mikrochemica Acta, 1955, 123; 1956, 869.
3. Pregl, Fritz, and Grant, Julius, Quantitative Organic Microanalysis.
4. Steyermark, Al, Quantitative Organic Microanalysis.
5. Wilson, Cecil, and Wilson, David, Comprehensive Analytical Chemistry.
6. Wiberley, J. S. Microchemical Journal, 1958, II, 219.

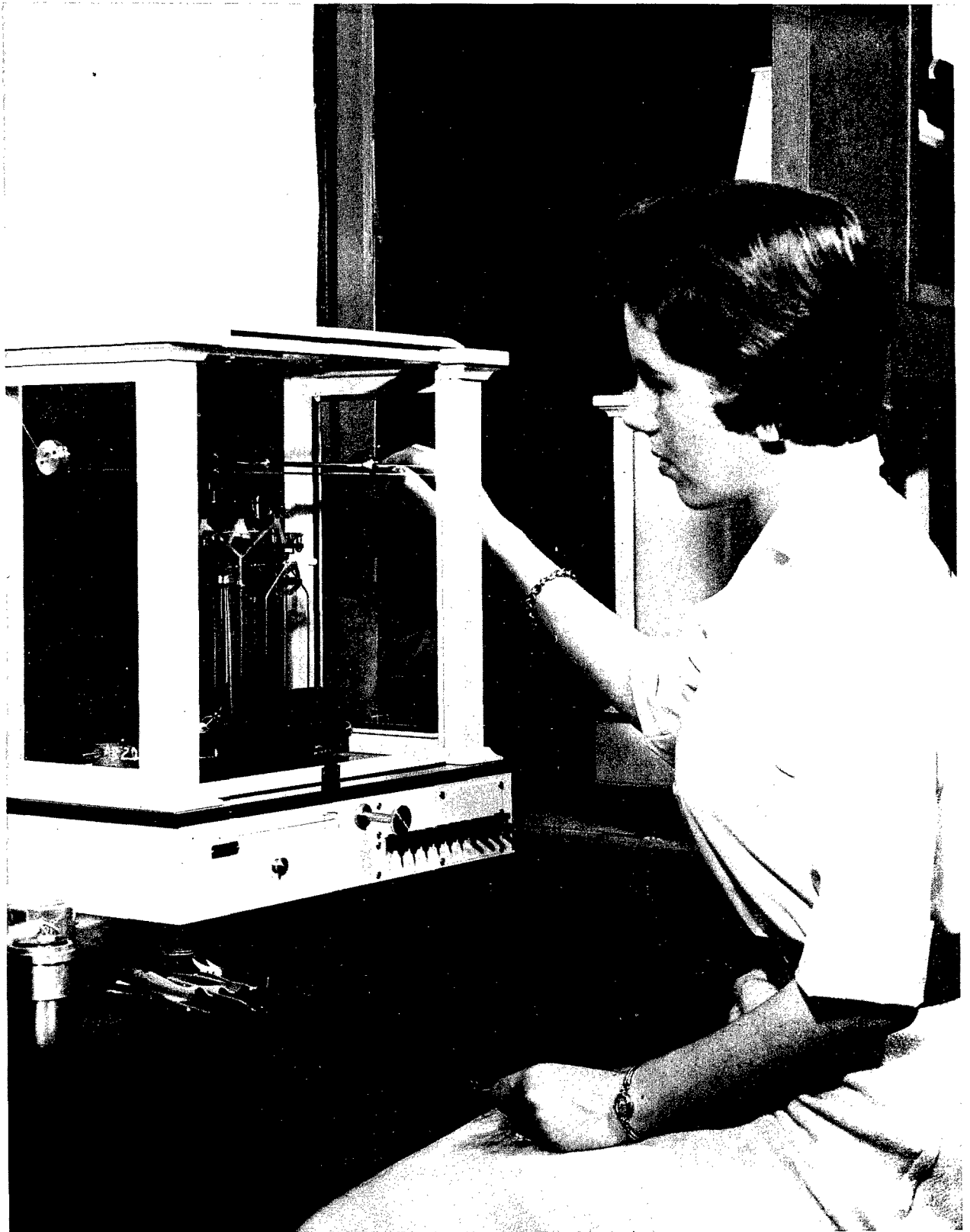


Figure 1.

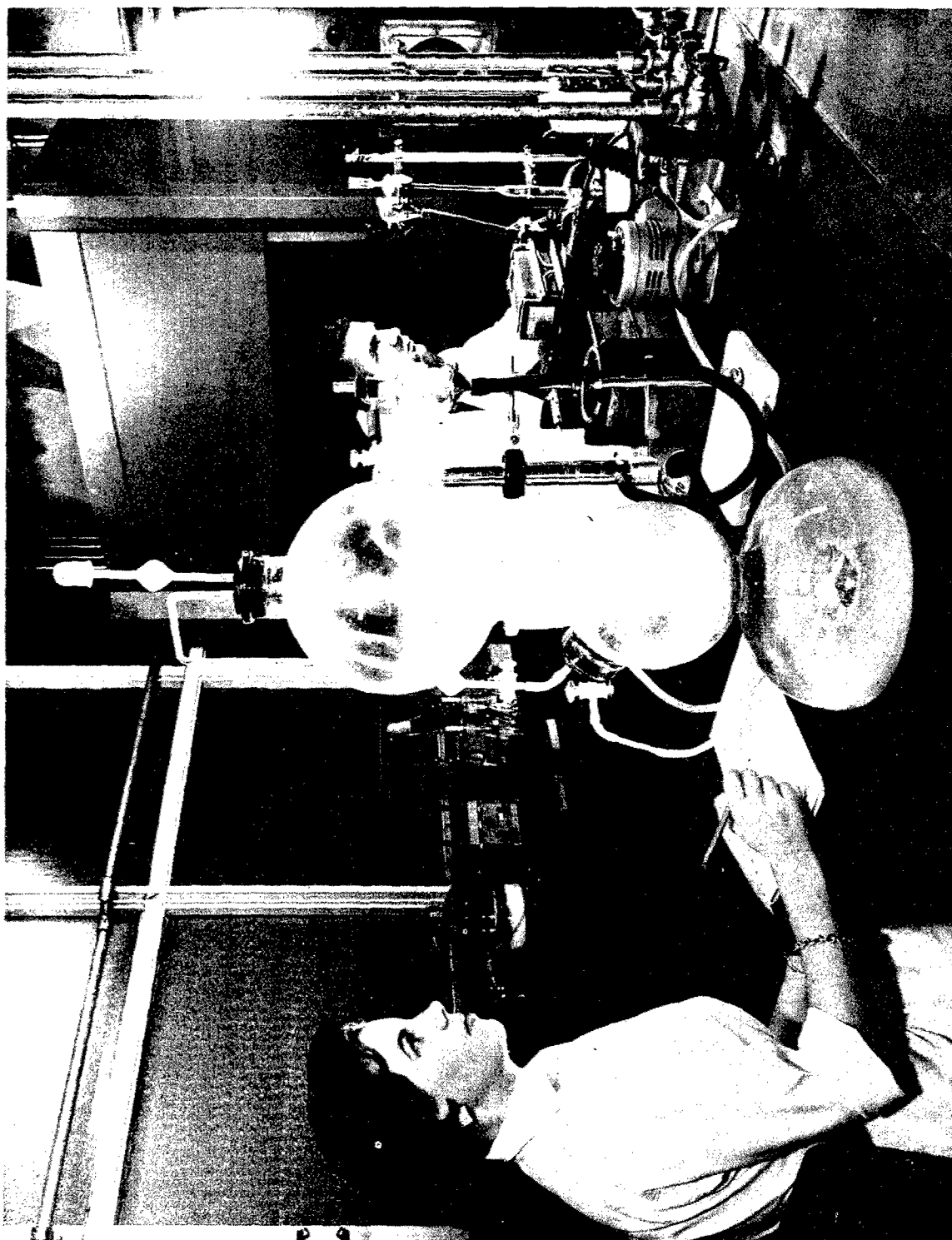


Figure 3.

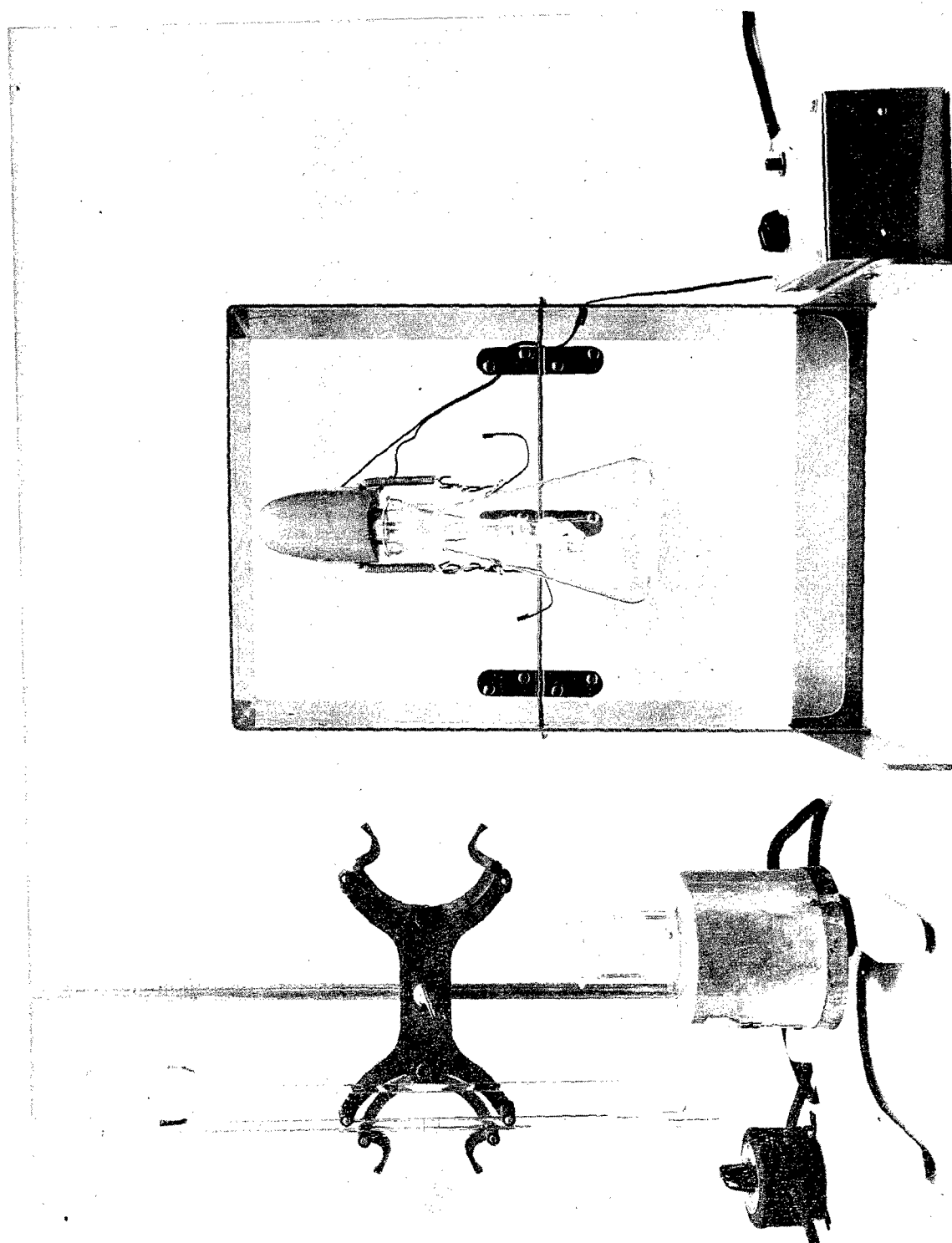


Figure 4.

X-RAY FLUORESCENCE ANALYSIS

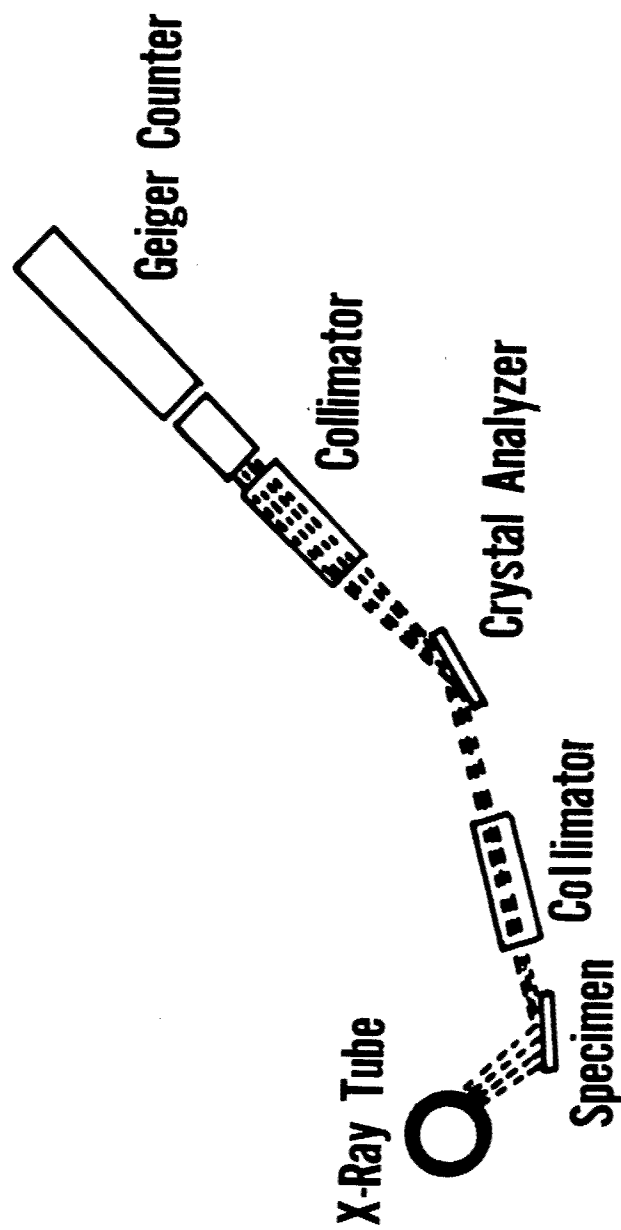


Figure 5.

NEUTRON MODERATION

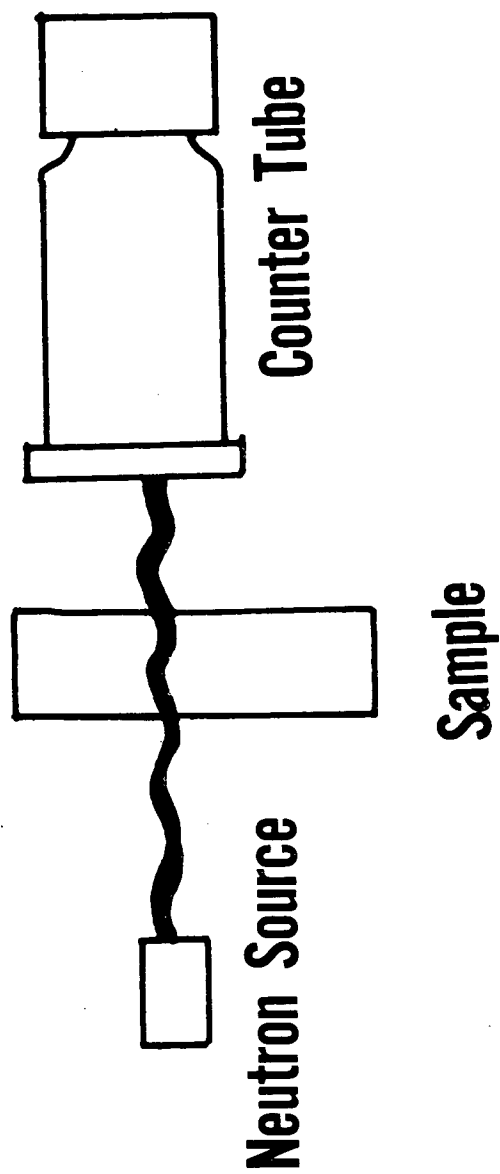


Figure 6.

CHEMICAL ANALYSIS OF SOLID STATE MATERIALS BY MASS SPECTROMETRY

William L. Baun

Directorate of Materials and Processes, ASD

Introduction

The mass spectrometer is a relatively old and established tool of analytical chemistry. Normally one thinks of the mass spectrometer only in terms of the analysis of gaseous species. However, recently the usefulness of the mass spectrometer has been extended to analysis of any materials regardless of their physical state. Therefore, in the very near future, advances will be seen in mass spectrometric analysis in at least three areas of work: (1) Qualitative and quantitative analysis of ultra pure materials such as conductors, semiconductors and insulators; (2) Structural studies on high molecular weight materials; and (3) Reliable identification of unknown materials by accurate measurement of molecular weight. Investigations in these areas had been severely limited because of inadequate commercial instrumentation, but instrumentation is now available to investigate the areas mentioned due to support by the Directorate of Materials and Processes of the development of a solid source, Mattauch type mass spectrometer by Consolidated Electrodynamics Corporation. This instrument and its uses will be discussed in this paper.

The Mattauch Mass Spectrometer

Mass Resolving System and Ion Path

The overall plan of the mass resolving system is seen in figure 1. Here we have an object slit behind which is situated the rf spark source; then a radial electric field which produces no mass dispersion, but which introduces velocity dispersion that closely compensates the velocity dispersion of the magnetic field that follows. The electric and magnetic fields act together to produce a mass spectrum in which the displacement of the ions is proportional to the square root of the mass. The radius of curvature in the electric sector is 25.188 inches, and in the magnetic sector the radius of curvature varies between 2 and 12 inches depending on the mass of the ion. The mass range of 36 to 1 on the photographic plate then allows coverage of all the solids in the periodic table in a single exposure. Much higher masses may be detected by changing the electrical and magnetic fields.

The next several figures are shown to acquaint the reader with the general appearance of the instrument and differences between this prototype instrument and the commercial model that is now being produced by Consolidated Electrodynamics Corporation.*

Figure 2 shows an end view of the instrument with the source housing in the foreground, the electric field sector further back, and the magnetic field and photographic plate holder in the background. Figure 3 shows the mass resolution system without gage and electronic panels, and figure 4, a close-up of the spark source. The knurled knobs on the source

* Consolidated Electrodynamics Corporation, 360 North Sierra Madre Villa, Pasadena, California

permit movement of either one or both electrodes during the sparking process. One degree of freedom that is not available in our instrument is movement of both electrodes back and forth in addition to the degrees of freedom, up and down and side to side. This would be very desirable since the ionization efficiency is dependent on the position of the electrodes in front of the slit system. Another near necessity which should be built into the source housing but is not in our instrument, is a high intensity light source for positioning electrodes preparatory to sparking. Figure 5 shows the spark source sample holder. Visible are the pin vise-type holders in which two pieces of the material to be analyzed are placed. These holders best accomodate flat samples about 1/16-inch thick and 1/4 to 1/2-inch long. A very desirable addition would be a set of claw-type holders which would allow the use of more irregular samples. Many facts of the instrument itself could be discussed further, but this short review will have to suffice.

Applications

Varied types of analyses have been made on this instrument, principally of the refractory metals, niobium, and tungsten. Although quantitative and semi-quantitative analyses have been accomplished with this instrument, it has been used mostly in qualitative analysis, where it is possible to identify on one spectrum all of the stable elements in the periodic chart. Further, every element has, within an order of magnitude, the same sensitivity, which makes comparison of one element with another more meaningful than in emission spectroscopy.

Such a survey spectrum of tungsten is shown in figure 6. Here, the photographic plate was shot in three sections, the top portion covering mass 7 through 41, the center portion covering mass 42 through 114, and the bottom portion covering mass 115 through 202. The tungsten is very impure even though prepared carefully from supposedly ultra pure tungsten hexachloride. Notable in the spectrum are lines due to multiply ionized tungsten.

To give an idea of the number of impurities to be seen in one tungsten spectrum, figure 7 was prepared with some thirty-two elements and compounds present in a sample of commercial tungsten rod. Lines due to compounds such as thorium dioxide and monoxide are seen, in addition to lines due to elemental species present in the sample. The appearance of ionized masses due to compounds is considered a distinct advantage, both in the analysis of purposely added dispersed second phases and in the detection of trace and minor impurities. In another tungsten sample containing 2.0 percent thoria, the mass spectrometric analysis gave the following amounts of thorium containing materials: Thorium, 1.90 percent, ThO, 0.10 percent, giving a total of 2.01 percent of elemental thorium and thorium compounds. Other analyses of dispersed second phases in tungsten which were investigated were B_4C , TaC, and ZrO_2 . Analytical results from these compounds were satisfactory, but in general not exceptionally accurate. However, it must be pointed out that these samples were not standards, but only wet chemically analyzed tungsten. More interesting perhaps, were inter-element effects occurring between the matrix, and additives with other elements, such as the formation of thorium carbides, tungsten oxides, and tungsten carbides. Figure 8 is a densitometer trace of a section of tungsten spectrum between mass 218 and 180 and shows the presence of WC, WC_2 , WO, and WO_2 . Note that oxides and carbides are seen for each major isotope of tungsten. Also the very broad lines between mass 180 and 186 which are the parent (plus one charged) tungsten ions. Even though this is a very strong exposure, minor components can be detected one mass unit from the parent tungsten masses. Also no trace is seen of any

mercury isotopes in this spectrum. We feel that since this is a mercury pumped system, it shows the effectiveness of the trapping design in the instrument.

One question that arises from data such as this is: did the tungsten originally contain oxides and carbides, or were these compounds formed in the vapor state between the electrodes? From the data taken thus far it appears that the answer to both questions is "yes" but, that most compounds seen are formed in the spark. To show the extent to which vapor state reactions do occur, electrodes of two different materials were sparked together. One such experiment used tungsten in one electrode and graphite in the other. Products which were identified were WC, WC₂, WC₃, WC₄, WC₅, WC₆, and WC₇. No tungsten oxides heavier than WO₂ have yet been identified, x-ray diffraction patterns taken of material sputtered in the source from the tungsten-carbon run showed the formation of one or more compounds which could not be identified.

Many such reactions are seen also when the same metal or compound is in both electrodes. Figure 9, for instance, shows some of the many compounds and associated elements formed in the spark of silicon carbide. Mass numbers are shown with the products to point out the formation of mixed dimers, trimers, etc. of isotopes of silicon. Many other mass numbers would be visible if mixed compounds of C¹³ containing products were visible in the spectrum. Abundances of some compounds were very small, so that every isotopic combination was not observed.

From the earlier tungsten spectrum and from the many products shown in figure 9, it becomes evident that high resolution is an absolute necessity in this sort of an instrument. Figure 10 shows a slow densitometer trace of a doublet at mass sixty due to Nickel 60 and Tungsten 180 having a plus three charge. The mass difference in this case is rather large, but it does serve to illustrate the sort of resolution possible using this instrument. The resolution of course could be made even better if a loss of sensitivity could be tolerated.

One set of elements in which resolution is not good enough to do isotope abundance measurements is the rare earth series. Figure 11 shows a densitometer scan of a run of Spex Industries' rare earth mix, which contains each of the rare earths. From this data we found that there are a number of rare earth doublets which are not resolved; this trace was run much too fast to detect resolution, if it were possible. Except for isotope abundance measurements, the mass spectrometer gave good results of rare earth analysis, and as can easily be seen from this trace which shows all rare earth lines, the spectrum is much simpler than that seen in emission spectroscopy. Just to show a comparison, figure 12 of an emission plate was prepared showing the emission spectrum of the same rare earth mix used in the earlier figure. The spectrum immediately below the rare earth mix is Yttrium.

The graphite matrix which is frequently used in our Laboratory to contain inorganic compounds for solid source mass spectrometric work has provided interesting data all its own. An interesting phenomenon observed in graphite mass spectra is "clumping" or the association of more than one carbon atom in ionized states. When a heavy exposure is made using only graphite electrodes as a source, a series of doublets is seen across the plate beginning at C₁ (which is one C¹² atom; or on C¹³ atom) and continuing to C₂₈ or twenty-eight carbon atoms. Probably more associations in graphite are possible, but

C_{28} is the largest mass seen thus far. It is interesting to note that the literature shows C_{28} as the top figure, also in work done by Dornenburg and Hintenberger.* The exact structure of these associated ions is not clear, but it appears that they are clumps, fragments, or chains of C_{12} atoms bound together. The doublet of "mass plus one" seen with the C^{12} atoms is about 1/100 as strong as the other peak and is ascribed to one C^{13} atom occurring in the carbon polymer, chain, or fragment. A plot of the intensity of these associated groupings agrees fairly well with data of Dornenburg and Hintenberger. Figure 13 shows both sets of data. Although both curves follow the same general pattern, several differences are evident. The most important difference in data is at C_3 where Dornenburg and Hintenberger show C_3 to be stronger than C_2 . Our data indicates that C_2 is much stronger than C_3 , so strong in fact that reversal occurred on the spectrum at this point and the intensity could not be measured. Also there is a slight difference at C_{18} which we measure as the high point in that region while the referenced authors show C_{19} to be stronger than C_{18} . Other types of carbon and carbon containing compounds are currently being studied to see if abundances are different in carbons and carbon compounds other than graphite. Interesting work of this sort is being done on the analysis of coal in the spark source in cooperation with the U.S. Bureau of Mines. Results of this work will be reported at a later time by A.G. Sharkey, Jr. of the Bureau of Mines, Pittsburgh, Pennsylvania.

In addition to investigations of association in graphite and hydrocarbons in coal, many different kinds of organics have been ionized in the spark source.

The technique used most for running organic materials in the spark source is as follows: graphite rods 1/8-inch diameter, spectrographic purity are drilled to a depth of about 1/2-inch with a No. 60 to No. 70 twist drill. The organic is then packed into the depression. Sometimes both electrodes contain samples and are pointed at the sparking rod. Usually only one electrode contains a sample and is left flat with a pointed counter electrode, just as in emission spectroscopy.

Another technique that is used and is more reproducible is mixing the sample with a good conductor such as silver, pressing it into a pellet, and using the pellet slivers as electrodes. Agreement between these two techniques is fairly good; but with the pelleting technique, frequently the organic compound and metal react in the spark to form a salt which adds a degree of complexity.

Various organic compounds have been run using one or the other of the techniques mentioned. In no system run thus far have we seen complete fractionation of the compound into only its elemental constituents. Many more relatively high mass fragments are formed than were originally predicted. Masses as high as 228 have been observed in organics, this particular one occurring in Ribose Nucleic acid. Other types of compounds which were ionized in the spark source are steriods, metallic salts, and urea adducts. Specific data will not be given on these compounds, but could be made available later upon request.

* Von E. Dornenburg and H. Hintenberger, Z. Naturforschg. 14a, 765-767 (1959)

The specific family of organics that will be described is the amino acid. Figure 14 shows most of the spectrum of an amino acid salt, L-lysine hydrochloride. As can be seen, many masses are present beginning at mass twelve and continuing well into the mass eighty region. Many doublets are present which probably cannot be seen in this figure. The total number of lines seen on the complete plate of L-lysine HCl was 101.

Figure 15 shows a plot of mass lines present in glycine, valine, phenyl, alanine, and L-lysine HCl along with masses from the matrix material, graphite. Since so many lines were present, including doublets and triplets, individual lines are not shown in this figure and intensities are not indicated. Many lines are present in each of the amino acids with only two similar gaps occurring in the spectra at about mass 19 to 23 and mass 31 to 35. Also it is interesting to note that glycine spectra shows many masses well above its molecular weight of 75, indicating many molecular recombinations, while valine and phenyl alanine show only one mass unit higher than the parent molecular weight, and no masses are seen in the lysine salt that even approach the parent molecular weight.

One of the most interesting results of these cracking patterns is the occurrence of the parent mass of the molecule and in addition, a line appears that is one mass unit heavier which apparently is due to the addition of a hydrogen to the amino group on the molecule. Usually the parent mass plus one is somewhat stronger than the line due to the parent mass, and in some spectra, only the parent plus one is seen. In all salts of amino acids investigated thus far, such as copper valine and L-lysine HCl, no parent masses of the salt are seen, and no parent-plus-one masses are seen. A more complete study on degradation of organic solids will be carried out upon the installation of a crucible source on the double focusing mass spectrometer. In this study we plan to compare thermal degradation of amino acids with effects seen in the spark source.

Within the next several months, the mass spectrometer will be equipped to analyze materials regardless of their physical state. The spark source, Knudsen cell capable of 2000°C, and the conventional gas source will be available. In addition, a Z-axis lens will be installed for focusing the ion beam which should increase the sensitivity by at least a factor of five.

This has been a quick survey of the various uses to which our instrument has been put. Other results on materials such as semiconductors have been obtained. Noted have been many advantages and some disadvantages of the system; generally, the advantages far outweigh the disadvantages.

Research Expectation in Mass Spectroscopy

At the beginning of this paper, it was mentioned that there appear to be several important areas of research in which mass spectroscopy should in the near future contribute heavily. Instrumentation such as that described, along with experimental models and commercial equipment* manufactured in other countries, will be used increasingly in analytical applications, structural studies, and measurement of molecular weights. Specifically, it is felt that a great deal will be done in the area of thermodynamics by use of the mass spectrometer equipped with crucible sources capable of temperatures up to 3000°K. This is an area in which both the Time-of-Flight Mass Spectrometer and the

* Associated Electrical Industries, Manchester 17, Great Britain

conventional mass spectrometer should make significant contributions in the thermodynamics of both inorganic and organic systems. Studies of ion-molecule reactions and electron-molecule collisions by the mass spectrometer should provide large advances in the theory of these processes. Of course, the greatest contribution of mass spectral analysis should be in the area of solids analysis in the parts-per billion range of any material of a complete insulator. Work in this area will undoubtedly flourish, and although the solid source mass spectrometer probably will never supplant the emission spectrograph, it may eventually be the only technique sensitive enough to analyze ultra pure research materials for the space age.

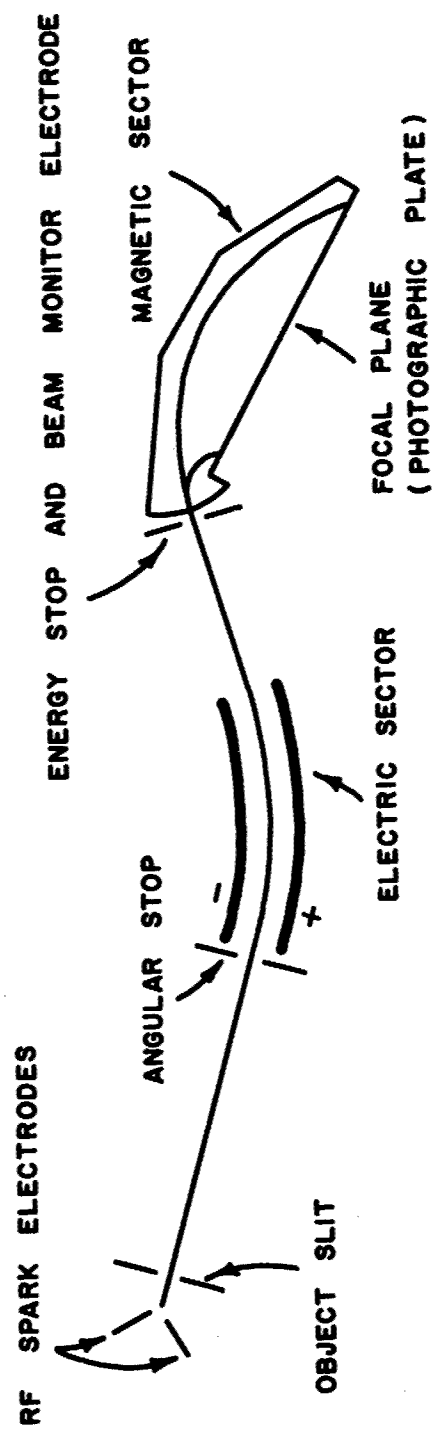


Figure 1. Schematic of Mass Resolving System

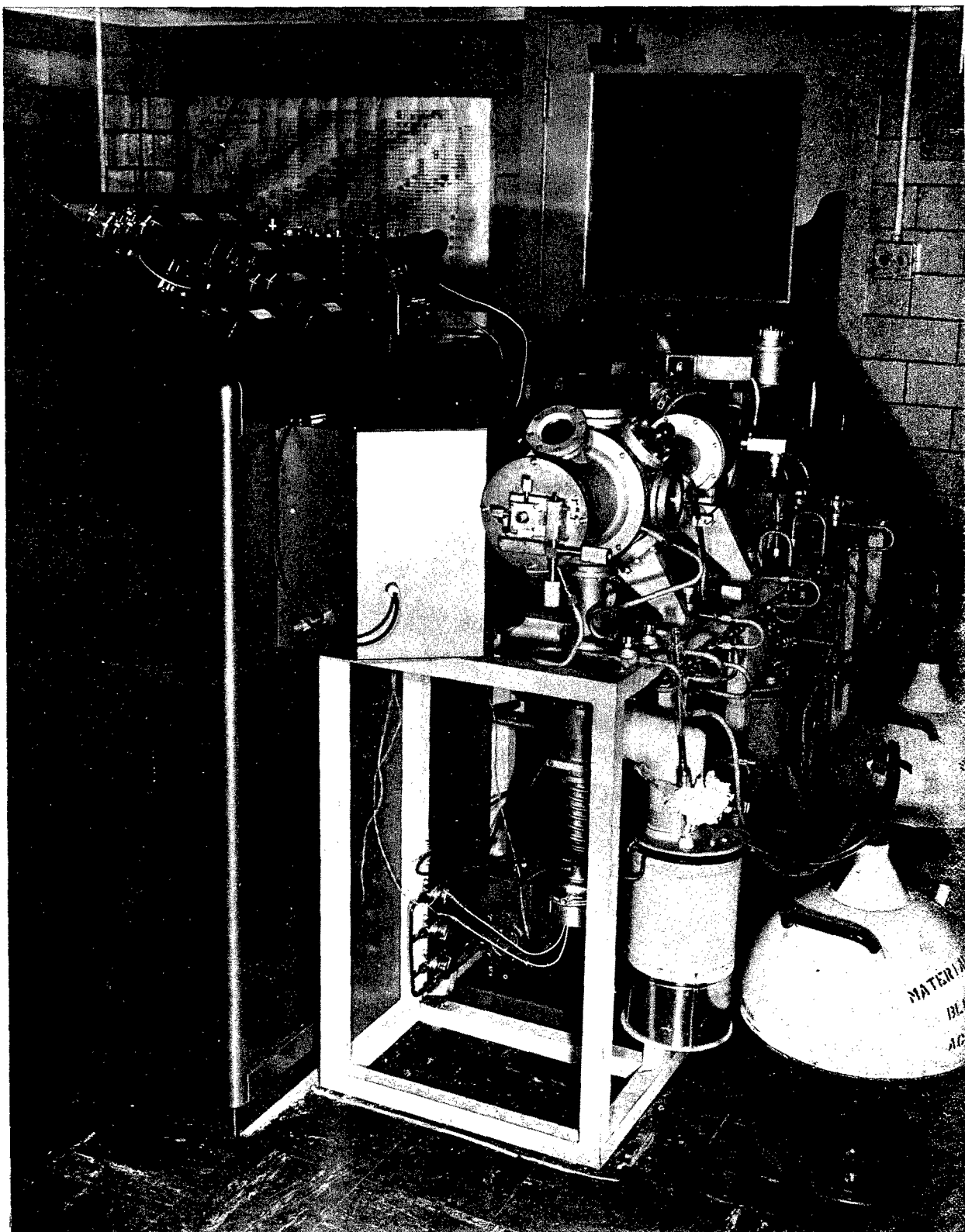


Figure 2. End View of Mass Spectrograph

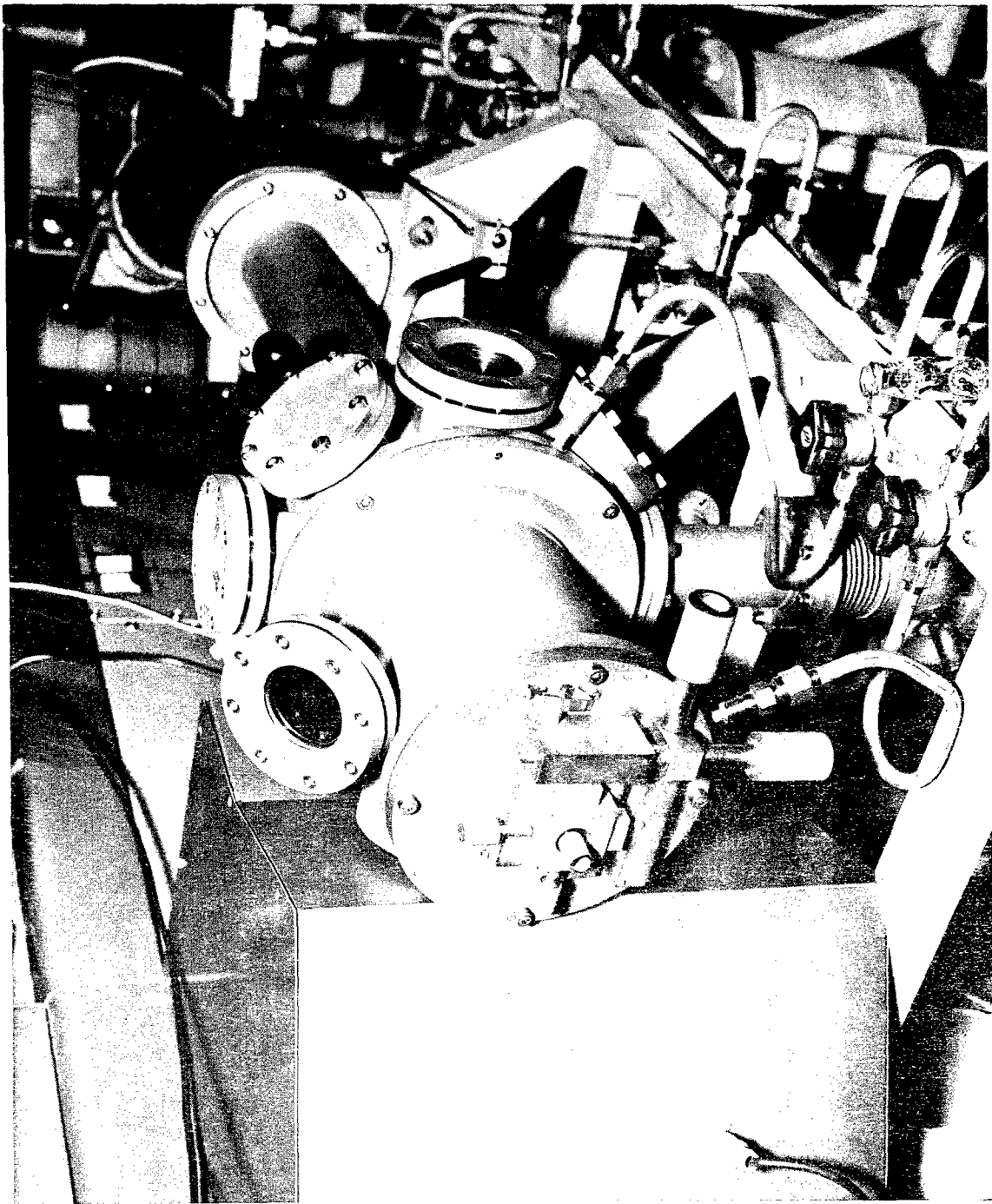


Figure 4. Closeup of Spark Source

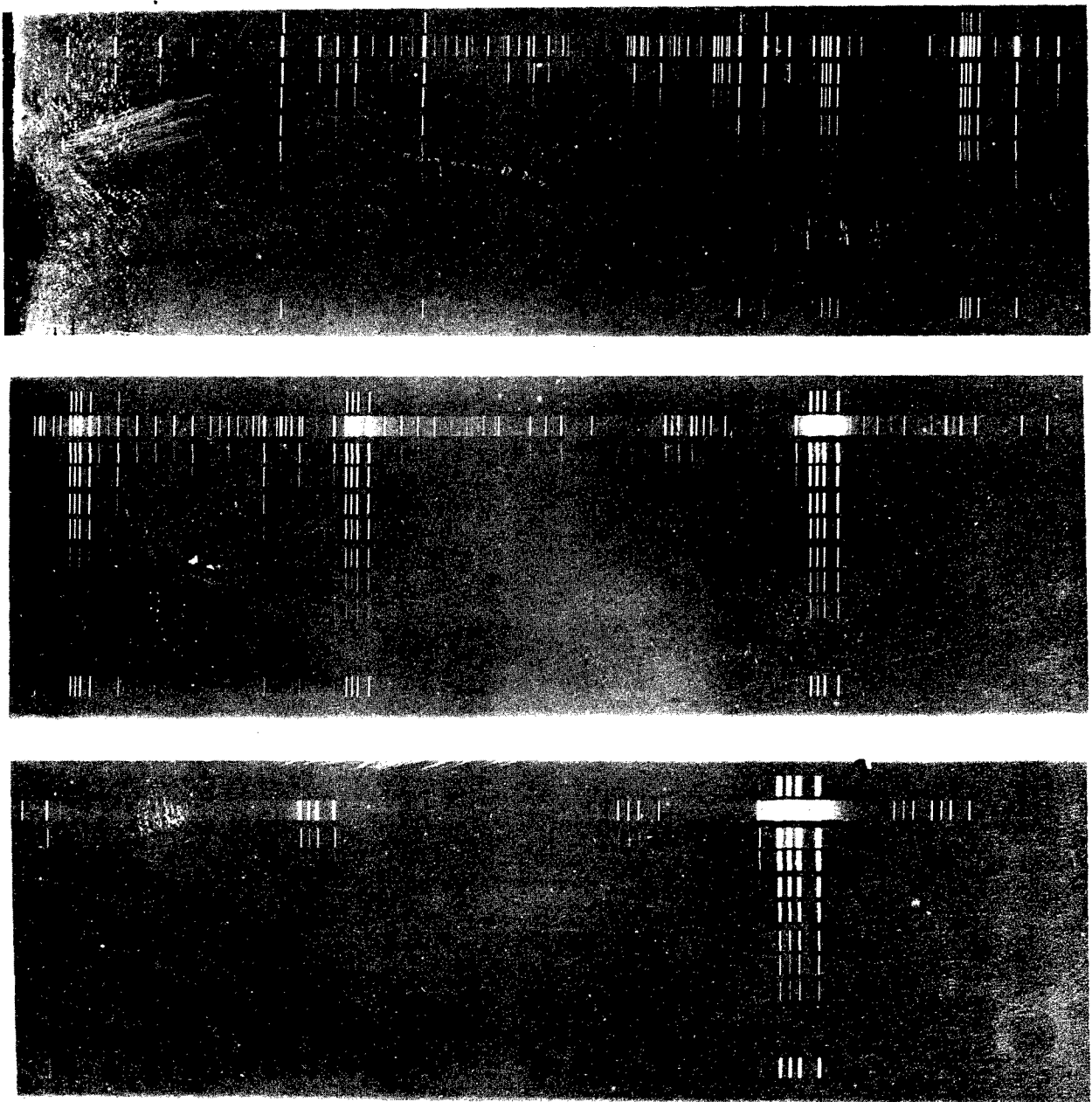


Figure 6. Survey Spectrum of Tungsten

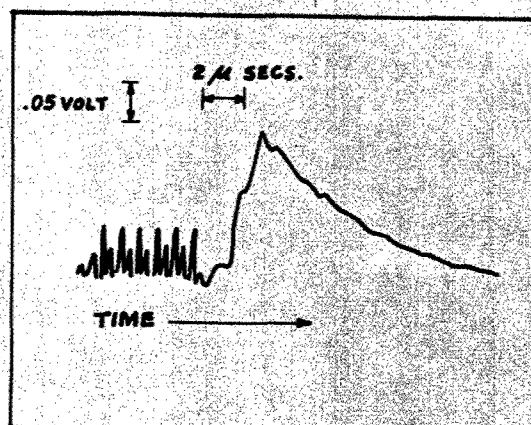
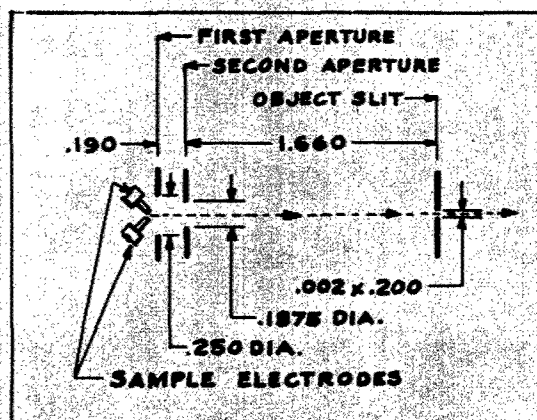
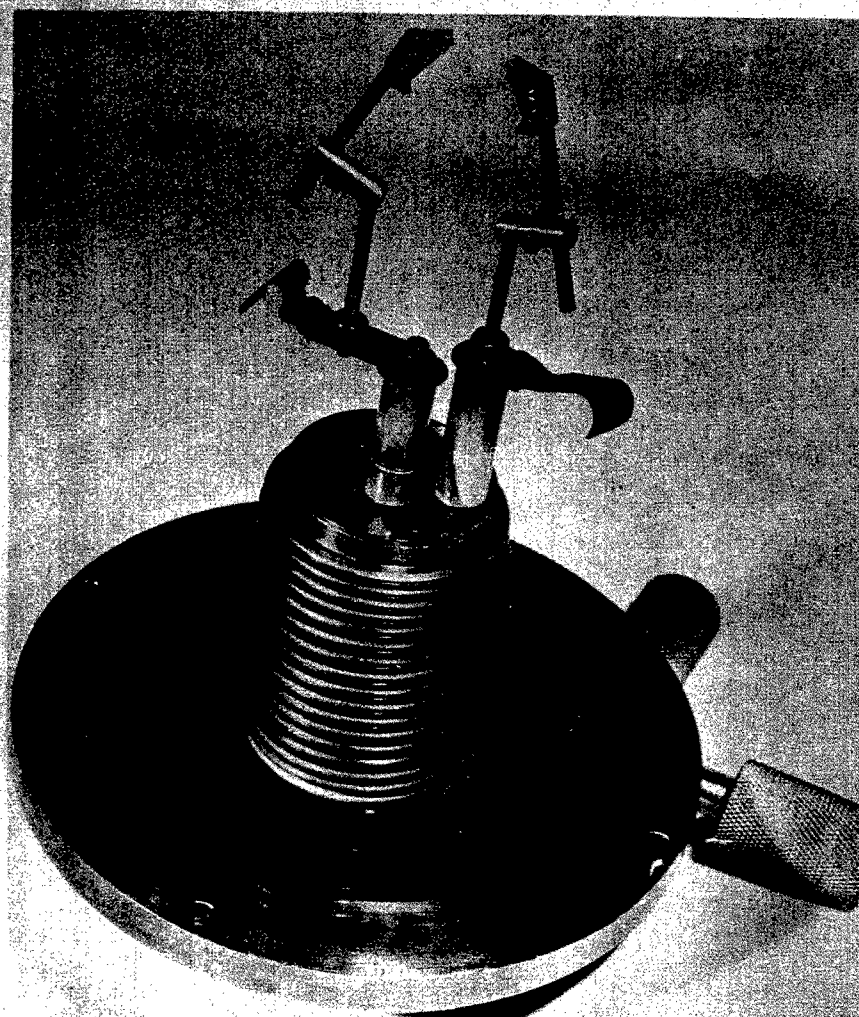


Figure 5. Spark Source Sample Holder

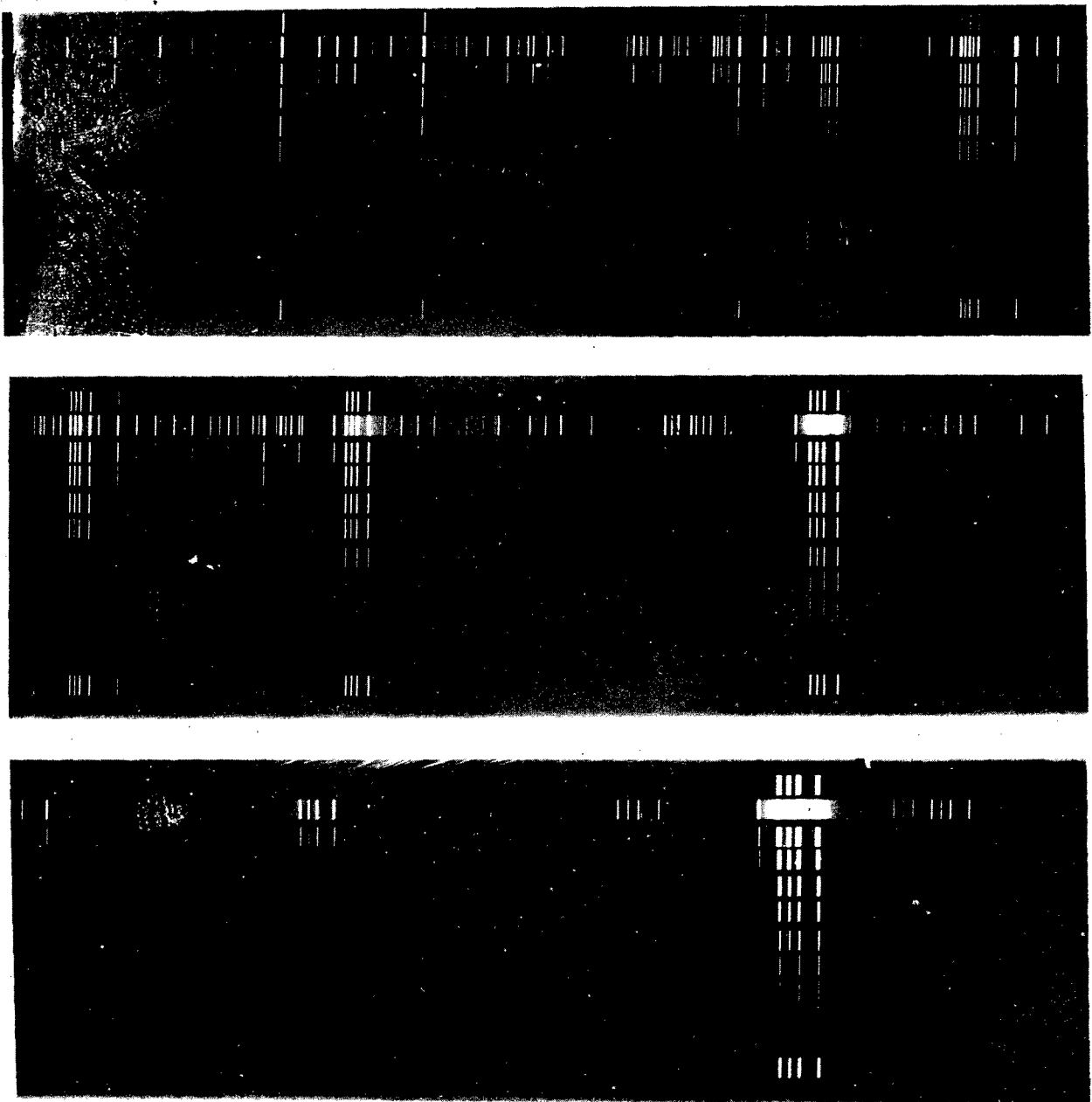


Figure 6. Survey Spectrum of Tungsten

ELEMENTS AND COMPOUNDS DETECTED IN COMMERCIAL TUNGSTEN ROD	
ELEMENT	CHARACTERISTIC LINES
THORIUM DIOXIDE	264
THORIUM MONOXIDE	248
THORIUM	232
LEAD	204,206,207,208
TUNGSTEN OXIDE	196,198,199,200,202
GOLD	197
TUNGSTEN CARBIDE	192,194,195,196,198
NEODYMIUM	142,143,144,145,146,148,150
CERIUM	136,138,140,142
TIN	112,114,115,116,117,118,119,120,122,124
INDIUM	113,115
SILVER	107,109
MOLYBDENUM	92,94,95,96,97,98,100
YTTRIUM	89
COPPER	63,65
NICKEL	58,60,61,62,64
IRON	54,56,57,58
MANGANESE	55
CHROMIUM	50,52,53,54
CALCIUM	40,42,43,44,46,48
ARGON	36,38,40
POTASSIUM	39,40,41
CHLORINE	35,37
PHOSPHORUS	31
SILICON	28,29,30
ALUMINUM	27
MAGNESIUM	24,25,26
SODIUM	23
OXYGEN	16,17,18
NITROGEN	14,15
CARBON	12,13
LITHIUM	6,7

Figure 7. Impurities in Commercial Tungsten Rod

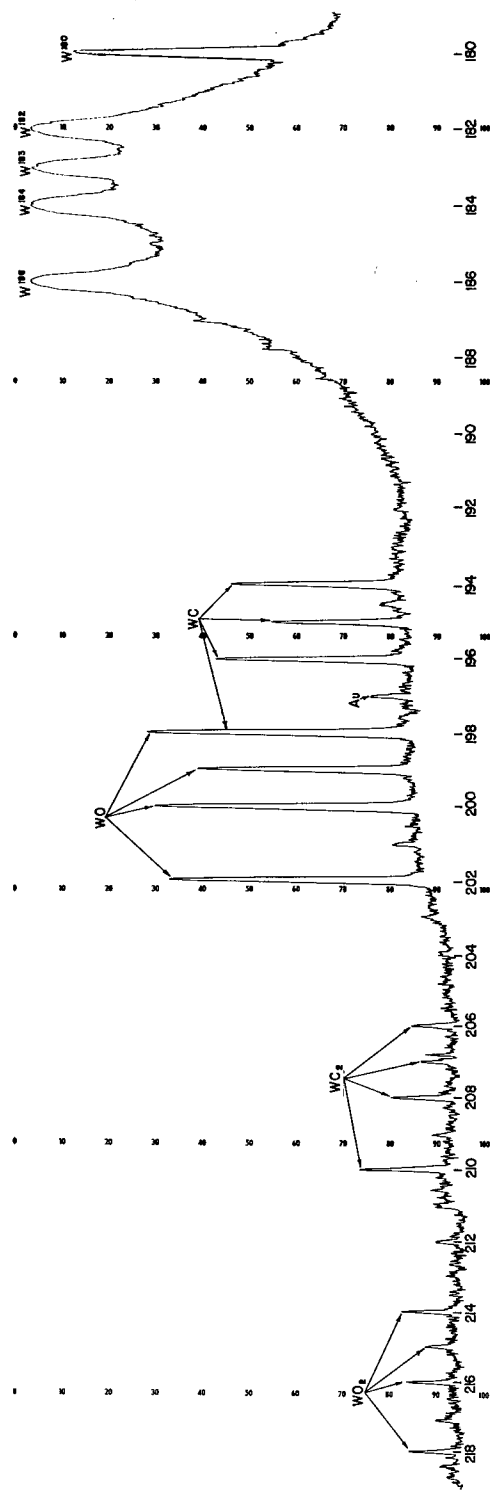


Figure 8. Densitometer Trace of Portion of Tungsten Spectrum

COMPOUND	MASS LINES VISIBLE
C	12, 13
Si	28, 29, 30
SiC	40, 41, 42
SiC ₂	52, 53, 54
Si ₂	56, 57, 58, 59, 60
SiC ₃	64, 65, 66
SiC ₄	76, 77, 78
Si ₂ C	68, 69, 70, 71, 72
Si ₂ C ₂	80, 81, 82, 83, 84
Si ₃	84, 85, 86, 87, 88, 89, 90
Si ₂ C ₃	92, 93, 94, 95, 96
Si ₃ C	96, 97, 98, 99
Si ₃ C ₂	108, 109, 110
Si ₄	112, 113, 114
Si ₄ C	124



Figure 9. Compounds Formed in SiC Spark

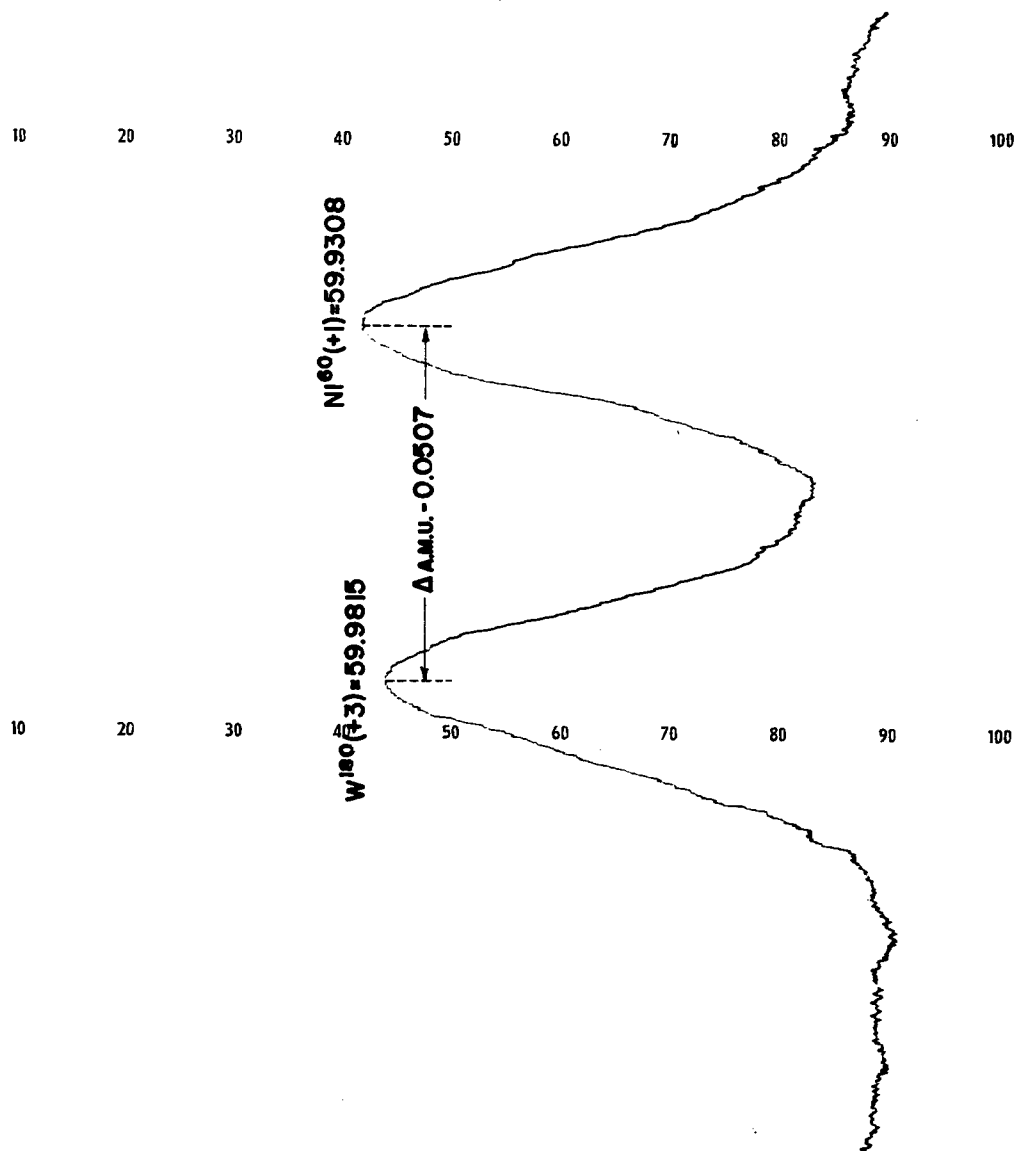


Figure 10. Densitometer Trace at Mass 60 (W^{180} 3 and Ni^{60} 1)

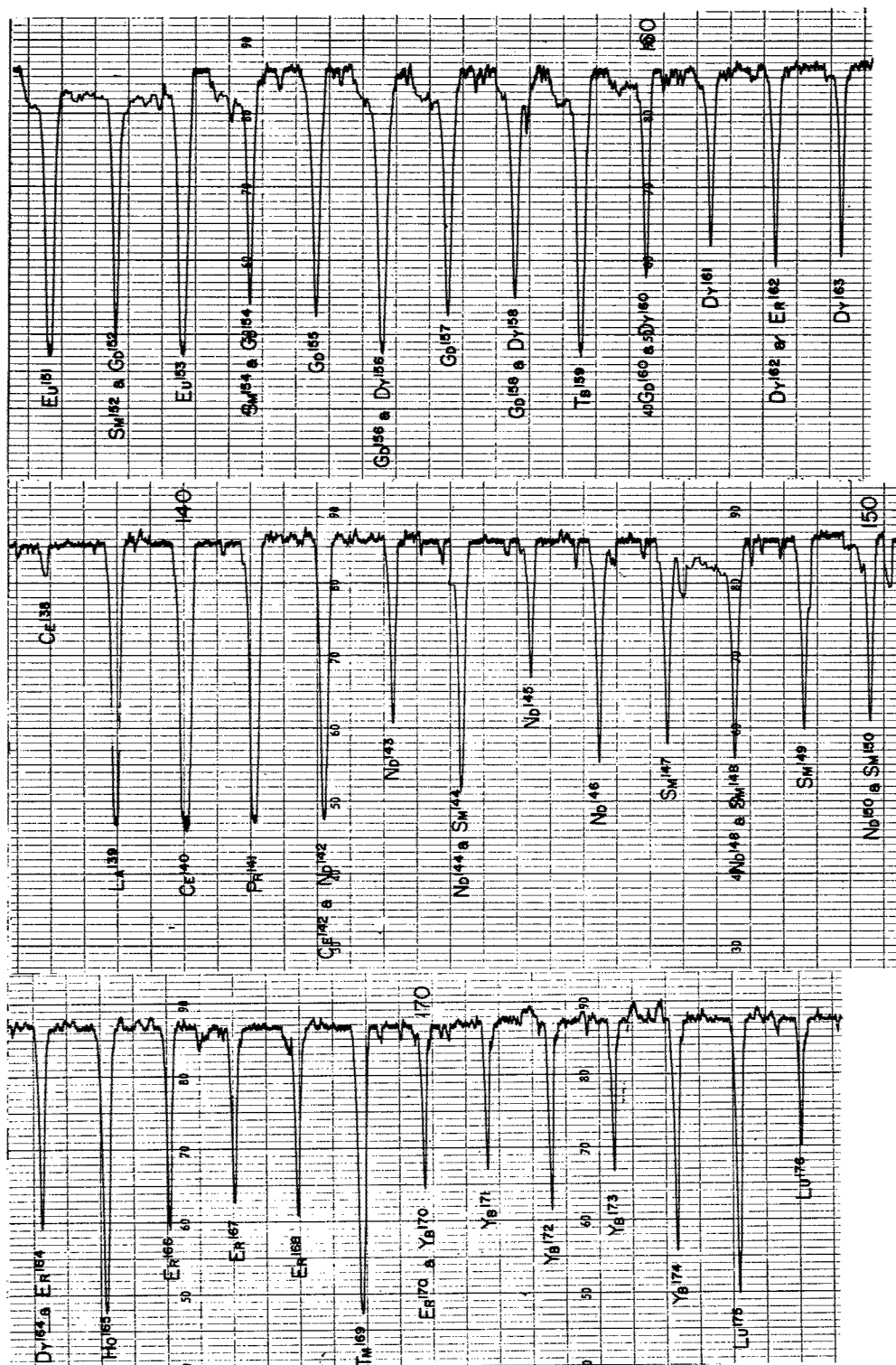


Figure 11. Densitometer Scan of Rare Earth Mix

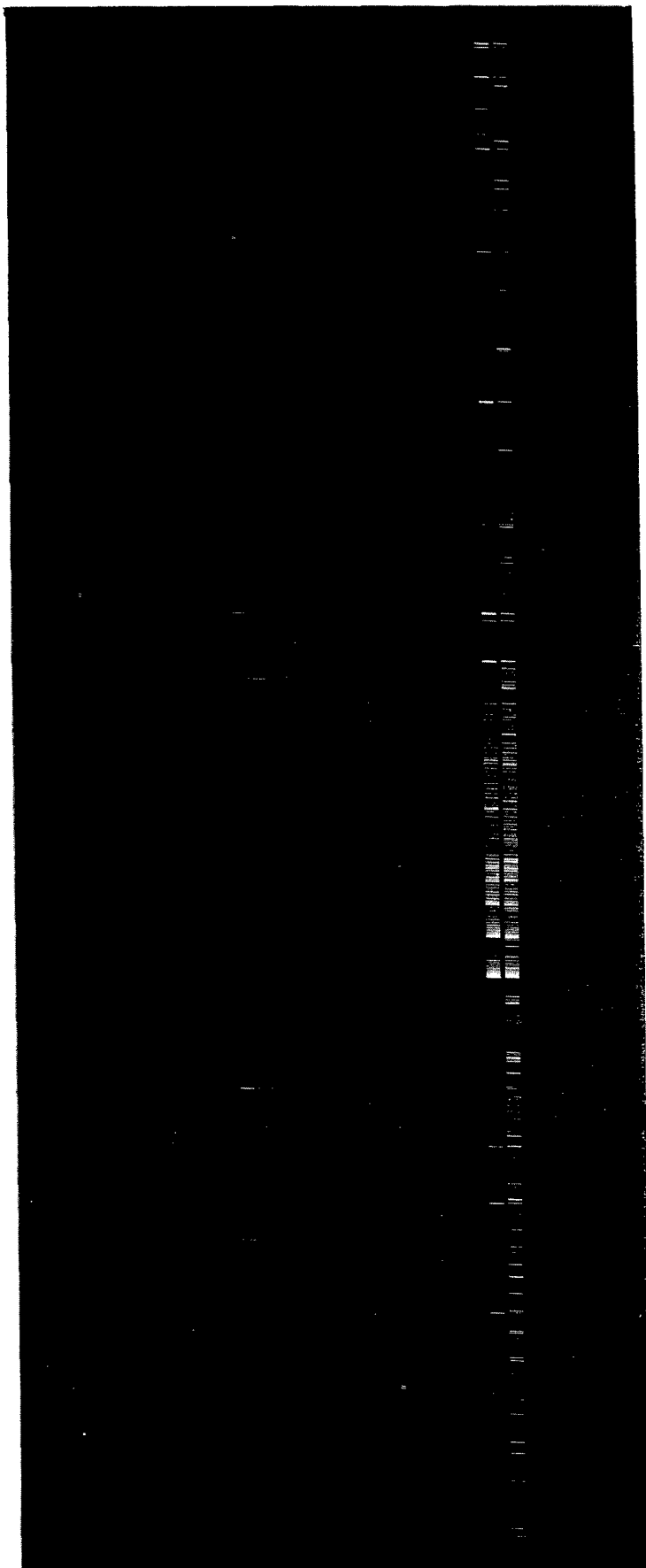


Figure 12. Emission Spectroscopic Plate of Rare Earth Mix

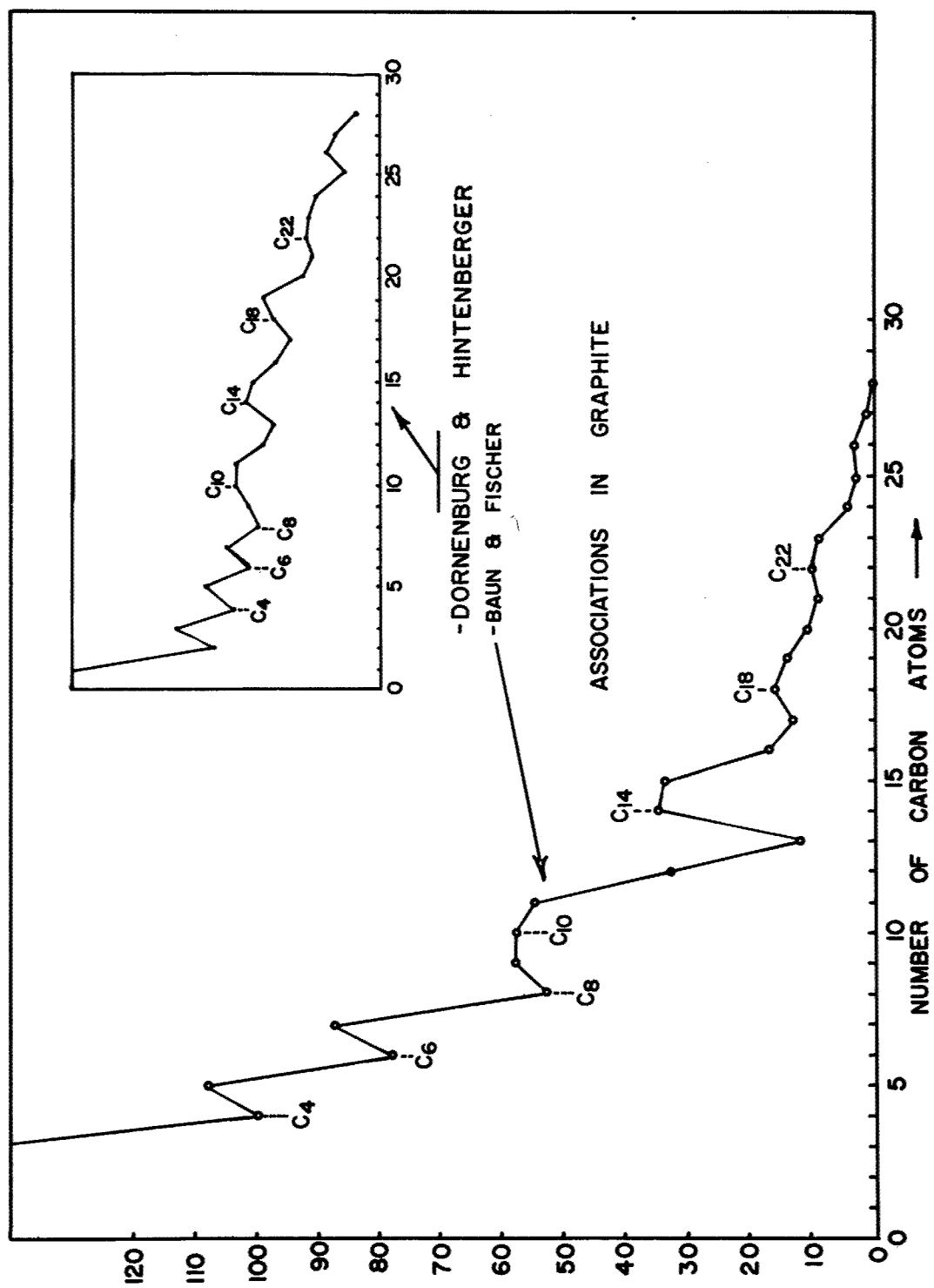


Figure 13. Association of Carbon in Graphite

L-LYSINE HCL IN GRAPHITE ELECTRODES

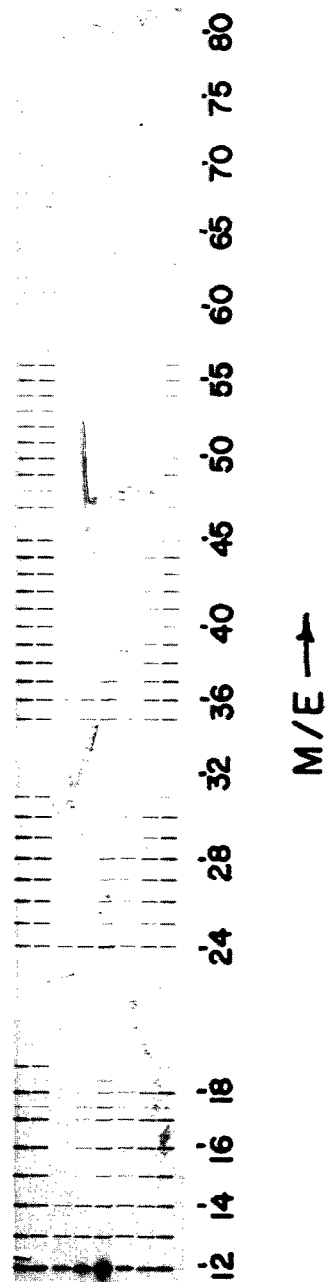


Figure 14. Mass Spectrum of L-lysine Hydrochloride

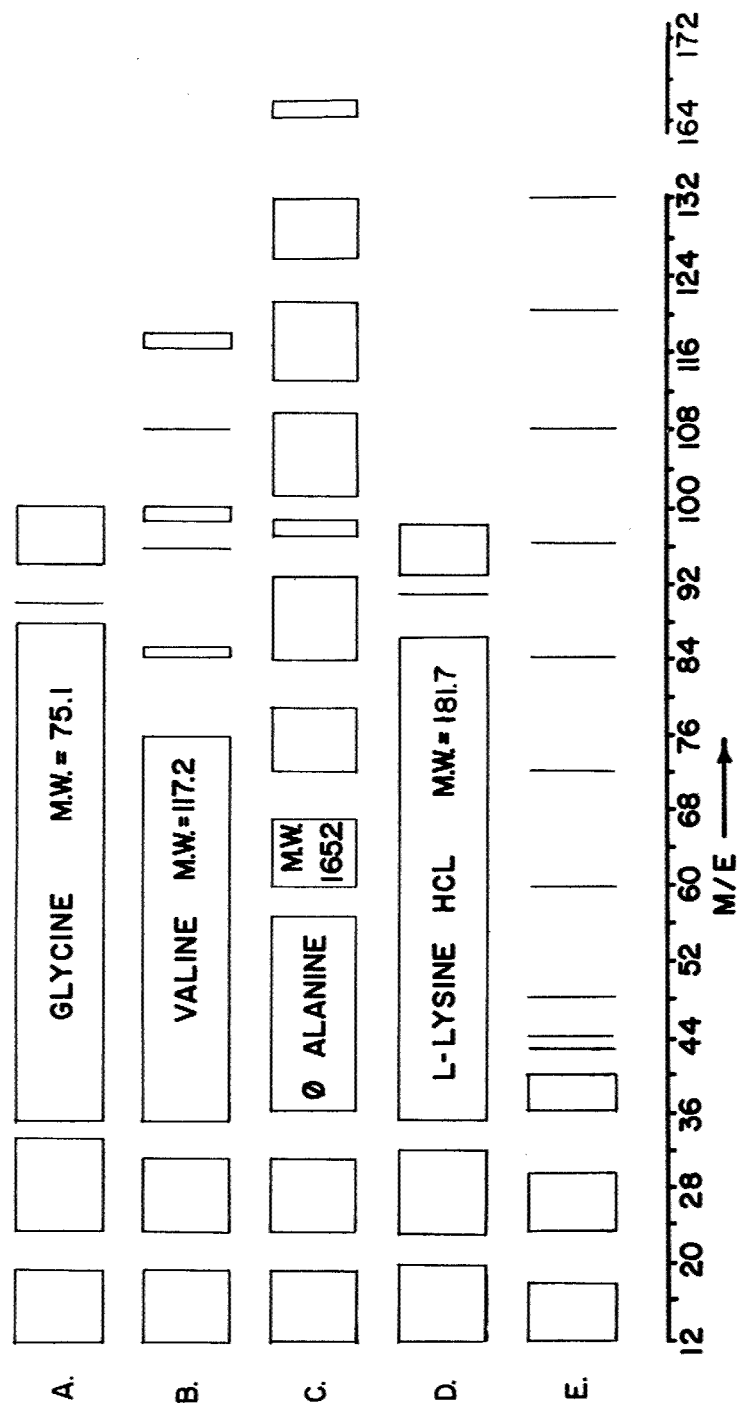


Figure 15. Masses Present in Amino Acids

THE FUTURE OF ANALYTICAL CHEMISTRY

Dr. L. Harrah

Directorate of Materials and Processes, ASD

The future of analytical chemistry is directed by current developments in materials research toward four general objectives. These four objectives, (1) increased precision, (2) lower limits of detectability, (3) finer detail in structural analysis, and (4) generalization and instrumentation of analytical techniques, are not qualitatively different from the requirements imposed on the analyst in the past. The magnitude of the effort needed in these four areas is, however, growing rapidly with the more stringent requirements being placed on materials behavior. The space environment, for instance, imposes a wide variety of conditions on materials used in the fabrication of vehicles and equipment.

To understand more fully the interactions of materials with their environments, it is essential that both the structure and composition of these materials be known. The mechanical behavior of bulk material may be dependent on components present in very small amounts or perhaps on very small differences in the quantities of the major components. Other properties may depend on microscopic and macroscopic arrangement of the various components. These questions of composition and structure are the problem of the analytical chemist, and it is essential that methods and techniques be developed to fulfill the current need.

Increased Precision

To increase the reproducibility of the results of any materials investigation, precision in composition must be achieved. The best methods of analysis in use today offer a precision of the order of one part in 10^4 while the current requirements in some cases are at least two orders of magnitude greater. In presently used instrumental techniques, such as emission and absorption spectroscopy, analysis with precisions of the order of one part in 10^3 are considered good.

Increasing the precision of absorption spectrometers can be accomplished by improving the signal to noise ratio and photometric accuracy of the overall instrument. To do this, one needs to study new, more efficient methods of converting the radiant energy signal into analytical information and more efficient, stable sources of radiant energy.

The problems associated with emission spectroscopy today are essentially problems of source instability. The dc arc source has the desirable characteristic of sensitivity but suffers from instabilities of many types. High voltage ac spark sources show greater precision than dc arcs, but suffer from loss in sensitivity and high continuous backgrounds. Various modifications of these two sources have been studied and some show promise for improved precision and reproducibility. Flame spectroscopy has perhaps the highest precision of any emission technique but still falls short of the requirements, one part in 10^6 . Extensive research on stabilization of emission sources together with continuous background reduction is necessary before this sensitive tool can be used in really precise work.

In designing equipment and developing new techniques for very precise analytical measurements consideration should be given to the analytical quantity from which the information is to be derived. Measurements involving the fundamental physical quantities, mass, length, and time, can be made with precisions of the order of 1 in 10^{6-7} , 1 in 10^8 , and 1 in 10^{8-9} respectively. Analyses based on these quantities can therefore be refined to high precisions. Analyses involving such derived quantities as volume, velocity, and voltage, will be inherently less precise. Consider the measurement of volume: if a length, L , can be measured with a precision of one part in 10^6 , the measurement of a volume derived from this length will be precise to only one part in $1/3 \times 10^6$. In general, derived quantities can be measured to an ultimate precision of $1/n$ of the precision of the quantities from which it is derived where n is the order of the derived constant with respect to these fundamental quantities.

Lower Limits of Detectability

In the fields of electrical and mechanical properties of materials and in biochemistry, the determination of extremely small amounts of impurities in large amounts of substrate is often required. To date, emission spectroscopy of trace metals has achieved perhaps the most general success and, in some cases, can detect and analyse traces of metals as low as one part in 10^{10} in solution.

Analysis of traces of impurities in ultra pure metals by emission spectroscopy is not as successful as we would like, particularly in materials of high atomic weight. Improvements in sources, particularly sources with low continuous background intensity, will allow lower limits of detectability. Application of fiber optics to emission spectrographs will allow large intensity gains by virtue of increased geometrical efficiency, but this will be useful only if the reduction in background intensity is first achieved so that the additional energy can be used.

Newer methods such as the high voltage ac spark source mass spectrometer show great promise in trace analysis. In contrast to emission spectroscopy, the mass spectrometer detection system is as sensitive for the detection of nonmetals as for metals. Although the spectra of elements of higher mass are somewhat more complex than those of lower mass, the great complexity of emission spectra is not observed, giving fewer interference problems and, consequently, greater ease in interpretation. The production of a continuous background in the mass spectrometer is more amenable to reduction methods than it is in conventional emission spectrography. The method is, however, applicable only to solids of relatively low vapor pressures that are either conductors or can be pelletized with conducting materials.

Atomic absorption spectroscopy, a relatively new tool for trace elements analysis, shows promise of increased sensitivity over emission techniques. Estimates of the ratio of emitting to nonemitting atoms in flame and arc sources give a value in the range of 1 to 500 . Since atomic absorption spectroscopy views these nonemitting atoms in the source rather than view the relatively small number of emitting atoms, a gain in ultimate sensitivity of about 500 is expected. In practice, however, since some of the nonemitters may exist in the form of molecules the sensitivity increase may not be realized. The greatest gains should be with atoms that do not tend to form strong covalent bonds.

These methods, emission spectroscopy and high voltage spark mass spectrometry, are jointly capable of trace analyses to very low limits, but they are destructive in nature and give information about elemental composition only. Analyses of trace molecular components are possible by these techniques only by inference. Techniques of equivalent sensitivity are needed for trace analyses of molecular entities.

Absorption and mass spectrophotometry combined with gas chromatographic separations have applications to analysis of trace quantities of molecular materials and are in some cases useful with sample sizes as low as 10^{-7} grams. They are, however, not directly applicable to trace analyses in large quantities of substrate without some prior separation. Extension of these standard techniques to lower limits of detectability is essentially a problem in development of new techniques of separation of the trace materials from the large quantity of substrate. Many specific procedures have been advised for these separations but are for the most part not useful as general techniques.

Research along the lines of general separation methods possible with quantitative interpretation such as is possible with vapor phase chromatography is desirable.

Structural Analysis

Perhaps the objective of greatest importance is the extension of analytical chemistry to the field of structural analysis. More and more frequently the analytical chemist is required to decide between a number of possible molecular structures for new synthetic materials. Combined application of such powerful new techniques as Nuclear Magnetic Resonance Spectroscopy and Electron Paramagnetic Resonance Spectroscopy with absorption spectroscopy can and will lead to greater understanding of the behavior of materials.

Extension of the readily accessible region of the electromagnetic spectrum of longer wavelengths into the infrared and microwave regions is desirable for study of secondary structural features of molecules such as chain conformation in elastomeric materials. High resolution long wavelength x-ray absorption and emission spectrometers, although not now routine tools, are capable of giving information about atomic position and, orientation in solids, liquids, and gases. Development of sources, detectors, and dispersing elements is particularly important to place these regions of the spectrum in routine use. In addition, extensive spectra-structure correlation work is essential before the spectra can be interpreted on an analytical basis.

Nuclear Quadripole Resonance Spectroscopy has been applied recently to problems of structural analysis in the solid state but has not been used as an analytical tool. Its disadvantage is that a single piece of equipment is applicable to only a few of the observable resonances because of the wide frequency range (50 kc to 3000 mc). The equipment needed to observe the resonance is not extremely complex and may well be very useful for particular analytical problems. A large number of resonances occur in the .5 to 150 mc range which may be covered by two or three units of more or less conventional radio communications equipment. Extension of this technique to analytical chemistry may prove quite profitable.

Many physical properties of matter have been used in general analytical methods. Among the more important are density, viscosity refractive index, and electric constant, and surface tension. These properties may be correlated with chemical structure and

used in structural analysis. There are many other physical properties, the Faraday Effect, the Kerr Effect, sonic velocity and transmission, to name only a few, which may be the basis for structural analytical techniques.

These measurements will, by their nature, have wide applicability once the basic correlations have been fully explored.

Generalization and Instrumentation

The increased demand for analytical services today places emphasis on rapid, accurate qualitative and quantitative analyses. New methods and modifications of standard procedures to reduce operator time in routine determinations are needed to meet this demand. Instrumentation and automation of determinations now accomplished by wet chemical means will allow the analytical chemist to devote more of his time to problems of a more complex nature.

Studies devoted to new methods with wide application to routine problems and which offer gains in speed and accuracy should not be neglected. Recent advances in instrumentation of elemental organic analysis by combining vapor phase chromatography and coulometric detectors with rapid combustion devices have cut down routine carbon-hydrogen analyses time to approximately 10 minutes, allowing 3 to 4 determinations in the time previously required for a single run.

Investigations of methods for other elemental constituents such as nitrogen and the halogens may offer equivalent gains. Perhaps polarographic analysis of combustion products absorbed in a suitable fluid may be rewarding.

Elemental organic analysis is only one area where instrumentation of analytical methods is needed. Ultimately, generalized instrumental methods should replace all types of routine analysis both organic and inorganic so that the aims of greater speed and increased accuracy can be realized.

MOLECULAR WEIGHT MEASUREMENT

Mary T. Ryan

Directorate of Materials and Processes, ASD

Introduction

The importance of molecular weight determinations in estimating the usefulness of polymeric materials has increased the emphasis in recent years on measurements used to calculate this value. The accuracy to which various colligative properties of solutions can now be measured has extended the range of these measurements from small molecules to compounds having molecular weights of hundreds of thousands. Of more importance to this Laboratory, is that increased accuracy also permits molecular weight determinations of new synthetic materials which have molecular weights of less than 1000 but which are only sparingly soluble in most organic solvents.

Ebullioscopy

Boiling point elevation or ebullioscopic measurements give the molecular weight of a compound through the following relationship:

$$\Delta T = \frac{RT_o^2}{L_e} \frac{\bar{V}C}{M}$$

where:

ΔT = boiling point elevation

R = gas constant

T_o = boiling point of solvent

\bar{V} = molar volume of solvent

L_e = molar heat of vaporization

C = concentration of compound in g/ml

M = molecular weight of compound

The 1919 invention of the Cottrell vapor lift pump made it possible to measure the actual boiling point of the solution making this measurement more meaningful. In recent years improvements in the design of ebulliometers to prevent super heating, the use of pressure regulators to avoid errors due to atmospheric pressure changes, and the use of new temperature detectors have greatly increased the accuracy of this measurement.

Using values for a typical solvent, $T_o = 353^\circ K$, $\bar{V} = 96$ cc, $L_e = 7.3 \times 10^3$ cal/mole, a concentration of 1 mg/ml of a compound having a molecular weight of 1000 will produce a boiling point change of $3.4 \times 10^{-3} ^\circ C$. While this temperature change is too small to be detected by a Beckmann thermometer, temperature differences of $6 \times 10^{-5} ^\circ C$ can be detected using thermistors (1). Using an 80 junction copper-constantan thermopile, the detection of a temperature difference of $1.5 \times 10^{-5} ^\circ C$ in an ebulliometer has been reported (2). However, the development of commercial instruments for ebullioscopic measurements to this degree of accuracy is lagging.

Cryoscopy

The freezing point depression equation for molecular weight determination is similar to that given above for ebullioscopy:

$$\Delta T = \frac{RT_o^2}{L_f} \frac{\bar{V}C}{M}$$

where T_o is now the freezing point of the solvent and L_f is the molar heat of fusion of the solvent.

For a typical organic solvent $T_o = 279^\circ\text{K}$, $\bar{V} = 89$ cc, $L_f = 2.4 \times 10^3$ cal/mole, so that a concentration of 1 mg/ml of a compound having a molecular weight of 1000 will produce a temperature change of $5.9 \times 10^{-3}^\circ\text{C}$, which can of course, be detected using thermistors, thermopiles, or liquid filled differential thermometers.

However, there are numerous solvents which have lower heats of fusion and would produce temperature changes more easily detectable, using the same concentration. The investigation and use of these solvents has not been fully exploited. Rast (3) demonstrated the use of camphor as a solvent. Cyclohexanol would produce a change of $.078^\circ\text{C}$, symmetrical difluorotetrachloroethane would produce a temperature difference of $.021^\circ\text{C}$ under the above conditions. The limited solubility of many of the new metallo-organic and inorganic polymers in the usual cryoscopic solvents indicates the desirability of determining the cryoscopic constants for other solvents, and developing equipment which may be used over a wide range of melting points.

Vapor Pressure Lowering

The addition of a substance into a solvent lowers the vapor pressure of the solvent. This vapor pressure lowering is measured indirectly in the ebullioscopic and cryoscopic measurements. The direct measurement of vapor pressure depression has not been widely used for molecular weight measurements because of the experimental difficulty in measuring small pressure differences.

The relationship between pressure change and molecular weight is:

$$\Delta p = P_o \frac{\bar{V}C}{M}$$

where P_o is the vapor pressure of the solvent and the other symbols are as given above.

At 40°C a concentration of 1 mg/ml of a compound of molecular weight 1000 in a typical organic solvent will give a vapor pressure depression in the order of 1.6×10^{-2} mm of Hg (2.1×10^{-5} atm).

An electronic differential micromanometer capable of measuring these small pressure differences was developed for Materials Central by the Arthur D. Little Company. This instrument uses a "microphone condenser" principle similar to that used in non-dispersion infrared analyzers. The pressure sensor contains an aluminized "Mylar" film diaphragm which separates the vapor above the solvent from that above the solution. This diaphragm is one plate of a condenser. The other plate is a fixed electrode mounted

a short distance from the diaphragm. This condenser is part of the tuning circuit of a self excited oscillator. The spacing between the electrodes which is determined by the pressure difference in the system causes a change in frequency in the circuit measured by a frequency counter.

A sensitivity of better than 50 cycles/micron is readily achieved. The frequency can be measured to ± 1 cycle/sec. The instrument is calibrated using an inclined oil manometer or using dilute solutions of compounds with known molecular weights. Vapor pressure depressions of 2×10^{-5} mm can be measured.

The cells containing the solvent and solution and the pressure sensor are immersed in an oil bath usually maintained at 40°C though other temperatures can be used if more favorable for the system being studied.

It is necessary to degas the system completely before making measurements. This is accomplished by freezing and pumping the system to a pressure of about a tenth of a micron, several times.

Figure 1 shows the cabinet containing the oscillator and frequency counter, the pressure sensor, and a cell which contains the solvent and four solutions of varying concentration with valves for isolation of the various solutions.

Figure 2 is a typical calibration curve. The sensitivity calculated from this curve is 56 cycles/micron.

Although considerable time is needed to make a measurement, the instrument is capable of good accuracy.

Within the last year or so an instrument which measures vapor pressure lowering indirectly at temperatures other than the boiling or freezing point of the solvent has become commercially available. The "vapor pressure osmometer" measures the temperature change caused by solvent vapor condensing on a thermistor containing a drop of a solution. Measurements can be made quickly and an accuracy of 1 percent for molecular weights up to 5000 is claimed. This instrument has been described by Hill (4) and Baldes (5) and by Neumayer (6).

Isopiestic measurements in which the solvent and solution are allowed to come to equilibrium in a closed system, and volume change used to calculate the vapor pressure difference will give the molecular weight. However, long periods of time are usually required to attain equilibrium.

Osmometry

The relationship between osmotic pressure and molecular weight is:

$$\pi = RT \frac{C}{M}$$

where π = osmotic pressure and the other symbols are as above. At a temperature of 300°K (R in gm.cm.), a concentration of 1 mg/ml of a compound of $M = 1000$ will produce an osmotic pressure of 25.4 gm/cm^2 ($2.5 \times 10^{-2} \text{ atm}$). This is by far the largest change in a measured value for the techniques discussed. Osmotic pressure changes are therefore more amenable to high molecular weight measurements. The retentiveness of the

osmotic membrane determines the minimum molecular weight which can be measured. Although 15,000 is about the lower limit for commercial gel cellophane membranes, recent experiments with other films indicate much smaller molecules can be retained.

We have used the Stabin modification of the Zimm-Myerson osmometer which is a high speed static type. A comparison between this instrument and its earlier modification indicates that the time required to reach equilibrium is only 1/6 th of that required with the earlier instrument.

In the discussion of various techniques, ideal solutions were assumed. Corrections for nonideality are normally needed, the simplest of which is extrapolation to infinite dilution. For osmotic measurements:

$$\left(\frac{\pi}{C}\right)_0 = \frac{RT}{M}$$

is usually used for calculations.

Other techniques for measuring molecular weights include end group analysis either by titration or quantitative light absorption analysis, x-ray analysis for crystalline polymers, light scattering, intrinsic viscosity and an ultracentrifuging. The latter three are usually applied only to very high polymers and do not give results directly comparable with the number average obtained from colligative properties.

REFERENCES

1. Dimbat, M. and Stross, F. H., Anal. Chem. 29, 1517 (1957).
2. Glover, C. A. and Stanley, R. R., Ibid. 33, 447 (1961).
3. Rast, K., Ber. 55, 1051 (1922).
4. Hill, A. V., Proc. Roy. Soc. London A127, 9 (1930).
5. Baldes, E. J., J. Sci. Instruments 11, 223 (1934).
6. Neumayer, J. J., Anal. Chem. Acta 20, 519 (1959).

EXTERIOR OF ELECTRONIC CABINET & ASSEMBLY

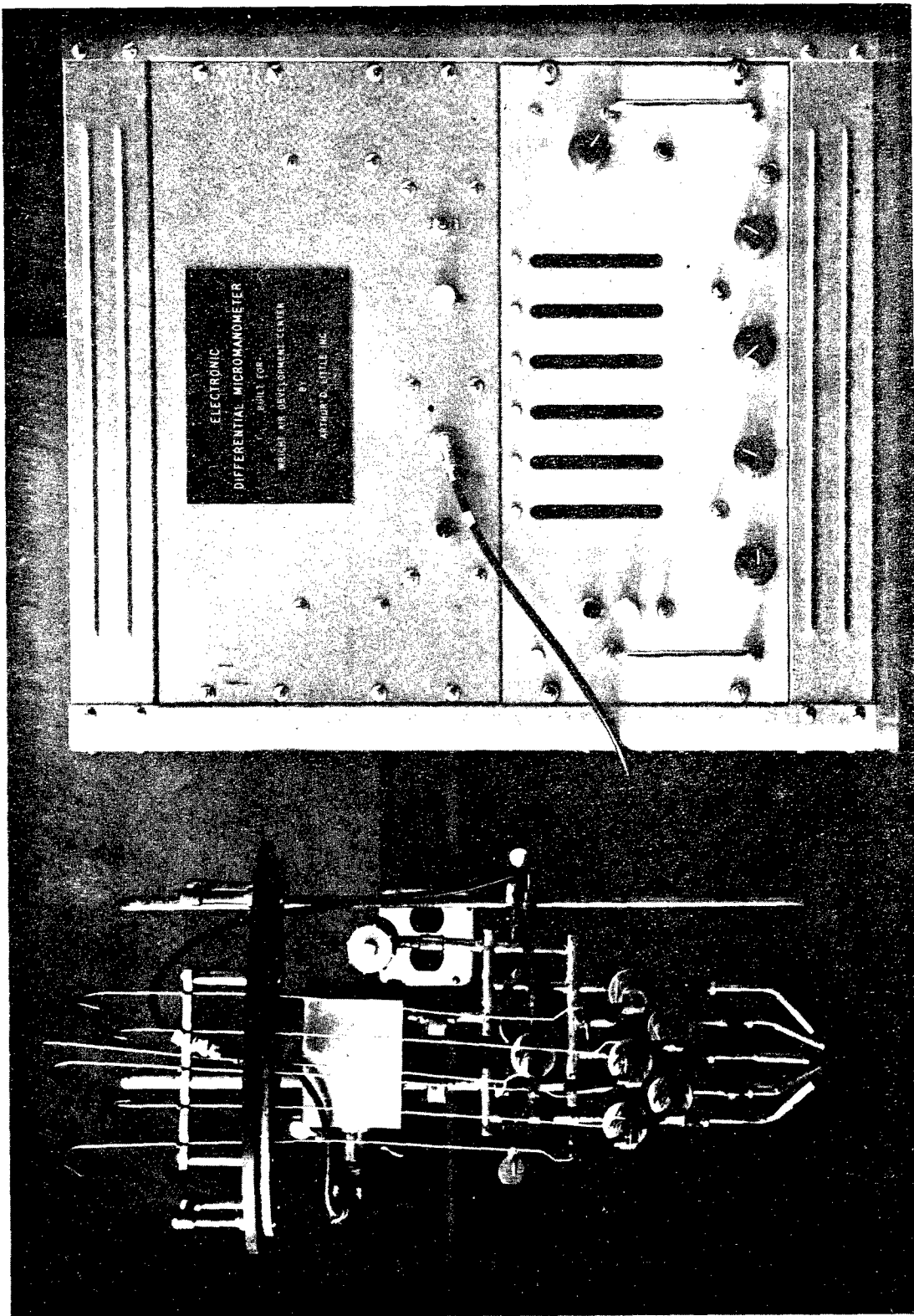


Figure 1.

PRESSURE IN INCHES OF WATER

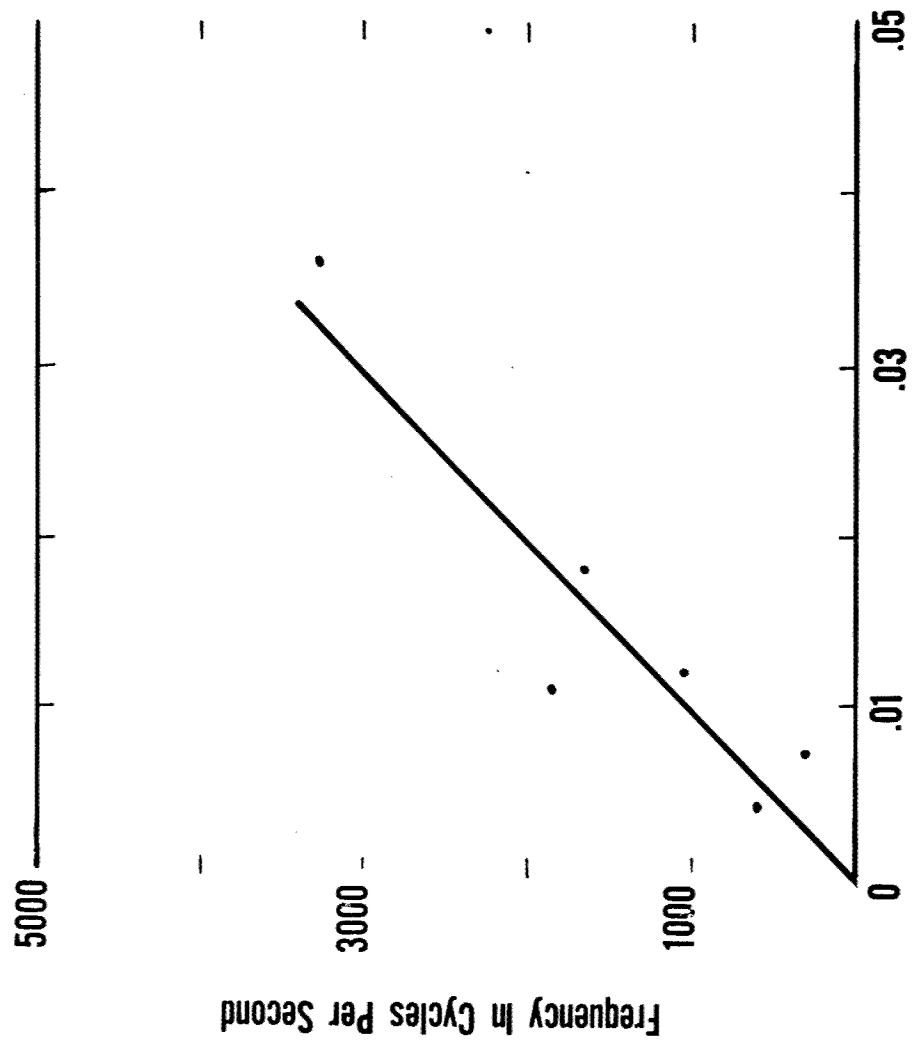


Figure 2.

MAGNETIC MATERIALS

Chairman

Dr. K. Strnat

Speakers

Mr. N. Korolkoff

Mr. J.C. Olson

Panel Members

Dr. C. Pitha (AFCRL)

Mr. J. Brauer

MICROWAVE FERRITES

Joseph B. Brauer
Nicholas O. Korolkoff

Electronic Materials, Rome Air Development Center

Introduction

It is apparent from the title that this paper will be concerned with a limited region in the entire spectrum of ferrite applications. Unfortunately, the region is one which may present considerably less economic interest to the manufacturer of ferrite devices when the production quantities of ferrite microwave isolators are compared to those of "fly-back" transformers, for example. Perhaps, for this reason, together with the inherent problems of higher frequency technology, the rate of progress seems slow in achieving ultimate utilization of microwave ferrites.

This discussion will be concerned with a definition of primary loss mechanisms in ferrites, materials properties which are significant to the performance of typical microwave devices, current trends in ferrite applications, recent progress and problems in materials, and some observations regarding future ferrite development.

To simplify discussion, the microwave ferrites are grouped functionally in table 1, which relates also the significant effect with the type of device application. Any discussion of ferrite applications, especially those at microwave frequencies, requires some mention of dielectric and magnetic loss mechanisms.

Dielectric Losses

If we differentiate between true dielectric loss and loss due to high electrical conductivity, it is the latter which is most significant to ferrite performance. Conduction by mixed valences is, today, cited as the principal cause of conductive losses. This mechanism is typified by the existence of divalent and trivalent iron (Fe) ions in a ferrite which is deficient in oxygen because of composition or sintering processes. Ascribing losses primarily to mixed valence mechanisms may be a gross oversimplification in most cases. The divalent Fe in a ferrite being sintered may form a solid solution or displace, from the spinel lattice, other divalent ions which form a second phase. This happens with magnesium (Mg) ferrite (1), in which the divalent ion displaces Mg ions from the spinel lattice which form separate crystals of Mg oxide (periclase), and result in a very high conductivity ferrite. A look at the phase diagram of most ferrites indicates a narrow region of oxygen content over which the composition can contain only a single spinel phase as indicated in figure 1 for nickel ferrite (NiFe_2O_4). For the Mg-manganese system, there is no region at all in the vicinity of the stoichiometric composition where a single spinel phase may exist (2). Closer examination may reveal that many of the ferrites reported to have high or peculiar loss properties and behavior were beset by polyphase problems which made either analysis or correction of the deficiencies extremely difficult. Some of the means employed to prevent the effects of oxygen loss have been:

1. Sintering in oxygen at the decomposition pressure of the ferrite or in other gases.

2. Use of additives such as copper (Cu) and vanadium (V) to reduce sintering time and/or temperatures.

3. Introduction of a small amount of an ambivalent ion such as Mg or cobalt (Co) which is more readily reduced at high temperature than is trivalent Fe.

4. Replacement of appreciable amounts of the Fe with another element such as aluminum (Al), which exists only in the trivalent state. This affects the resultant ferrite in several ways; it increases the lattice stability, decreases the available oxygen which can be lost during sintering, and introduces interfering ions in the easy conducting paths which may otherwise exist.

Magnetic Losses

In ferrites, there is the familiar domain structure in which the elementary dipoles are all aligned and adjacent domains are separated by boundaries (termed Bloch walls) in which the spins gradually change direction. The wall has a thickness dependent upon conditions for minimizing the damping associated with spin exchange energy and the anisotropy. Magnetization of a ferrite results in alignment of the magnetic vectors with the applied field and growth of those domains favorably oriented with respect to the field. The effective permeability of a ferrite is the result of both effects, domain wall movement, and domain rotation.

Pringle (1) gives the following treatment for ferrites at microwave frequencies:

The initial permeability, μ_i , has real and imaginary components due to damping forces and is usually expressed as

$$\mu_i = \mu'_i - j\mu''_i$$

Where damping is small at low frequencies ($\mu''_i = 0$) we can write:

$$\mu_i - 1 = 4\pi M_s^2 \left(\frac{1}{ad} + \frac{2}{3M_s H_e} \right)$$

Here a and d represent constants involving the stiffness in domain wall motion and domain size, respectively, M_s is the saturation magnetization, and H_e is the effective internal field within a domain. Polder and Smit (3) show H_e to lie between the value of the anisotropy field, H_{anis} , and $(H_{anis} + 4\pi M_s)$. H_{anis} is given by $4K_1/3M_s$ where K_1 is the first order crystalline anisotropy constant. Referring to the above equation, then, it can be seen that the first term represents the contribution due to domain wall movement and the second that due to domain rotation. Both processes lead to resonances in the μ''_i frequency spectrum. Rado, et al. (4), gives the resonance angular frequency for domain wall movement as:

$$\omega_1 = \gamma(8\pi a)^{1/2} (A/K)^{1/4}$$

where γ is the gyromagnetic ratio and A the exchange interaction energy per unit volume. Snoek (5) shows that the resonance angular frequency for pure domain rotation (from $\omega_2 = H$) is

$$\omega_2 = \frac{8\pi\gamma M_s}{3(\mu_i - 1)}$$

where μ_i is the initial permeability at low frequencies.

"The condition for elimination of low field loss in an unsaturated ferrite medium is $f > f_{lim}$ where

$$f_{lim} = \frac{\gamma}{2\pi} (H_{anis} + 4\pi M_s)$$

For high field devices the limiting frequency is that at which the field required for resonance equals the saturation field, and this is intimately connected with ferrite geometry."

In general, the magnetic losses in devices employing modulating fields in the hundreds-of-kilocycle to tens-of-megacycle range can be categorized as primarily domain resonance losses at low fields and hysteresis losses at high fields (near saturation). Both of these arise from "stiffness" of the domains and domain walls. Hysteresis losses may be reduced by reducing anisotropy although the low field losses may remain high for a particular frequency due to resonance in domain rotation or wall motion. The anisotropy constant K_1 can be minimized by employing a ferrite with a low Curie Temperature such as the nickel-zinc ferrite (6), or by adjusting composition in a solid solution of two ferrites with anisotropy constants of opposite sign. Typical of this technique is the NiCo ferrite system (7) which uses a small amount of Co ferrite with a large positive K_1 in a Ni ferrite solid solution of a small negative K_1 .

Low Field Devices

Devices based on the first effect, Faraday rotation (table 1), can be considered, in general, as low field devices. The low frequency limit in low field devices can be extended only by reducing both the saturation magnetization and the anisotropy (see the Polder and Smit relation, 3). One method of reducing the saturation magnetization is to substitute a nonmagnetic ion for part of the Fe (as in the ferrite aluminates).

High Field Devices

To eliminate low field loss in high field (resonance) devices, H_{sat} must be less than H_{res} and the condition for zero low field loss becomes $\omega > \gamma H_{anis}$. In a typical Ni ferrite with $\gamma = 3.22$ Mc/s/oersted and H_{anis} of about 400 oersted, the minimum frequency is about 1300 Mc/s. Lax (8) writes a relation for maximum reverse-to-forward ratio in a resonance isolator at a frequency, f , as

$$R = \frac{(4f)^2}{\gamma \Delta H}$$

which shows the importance of narrow line width at low frequencies for a given front-to-back ratio. Broadband applications require broad line width ferrites with fairly low γ , and narrow band applications with high back-to-front ratios require ferrites with narrow line width and low γ . Pringle reports X-band isolators with power ratios in excess of 120 to 1 using a ferrite such as $Ni_{0.975}Co_{0.025}Fe_2O_4$. More recently, ferrites such as Trans-

Tech414 have been used in X-band isolators and exhibit 20 to 40 db isolation (depending on power levels) with $\frac{1}{2}$ to 1 db insertion loss, respectively.

In high power devices, we must account for nonlinear effects, as illustrated in figure 2, for a typical resonance isolator investigated by Pringle, which employs MgMn ferrite strips against the broad faces of a rectangular wave guide. Lowering and broadening of the resonance absorption peak and the appearance of a subsidiary absorption peak are explained by Suhl (9) as being excitation of higher order spin wave modes which grow exponentially at the expense of uniform precession when the rf field exceeds a certain threshold value. The threshold for saturation of the main resonance peak is given by

$$h_{crit} = \Delta H \sqrt{\frac{2\Delta H}{4\pi M_s}}$$

indicating the desirability of broad line width ferrites if these absorption anomalies are to be avoided.

High peak power applications thus require broad line width ferrites with a high Curie temperature (for high average powers); and, high power continuous wave (CW) applications indicate the additional need for high resistivities.

Intermediate Field Devices

Nonreciprocal phase shift is based on the interaction of the microwave magnetic field with the Larmor precession of the magnetization of a ferrite which is biased with a dc magnetic field. Figure 3 shows typical phase and attenuation characteristics plotted as a function of the dc field strength. Such nonreciprocal devices as isolators and circulators make use of the difference in propagation constant for positive and negative circular polarization. The variation in propagation with applied field is used in switches and modulators.

In nonreciprocal phase shift devices, the fields must be large enough to saturate the medium but must be well removed from the resonance peak. Ignoring low field losses, Lax gives a relation for the maximum figure of merit (in terms of differential phase shift-to-loss ratio) at a frequency, f , as

$$F_{max} = \frac{2f}{\gamma \Delta H}$$

At lower frequencies (figure 3), there is more overlap of the low field losses and resonance losses. The amount of overlap can be reduced by using material with a narrow resonance line width. Because of the low field losses, the figures of merit involving only line width are inaccurate below S-band, and ferrites for use in this range should also exhibit low saturation magnetization. In transverse devices operated above S-band, the ferrite is usually saturated so that resonance loss predominates; this makes a narrow line width of primary importance.

Devices Using Nonlinear Effects

In ferrimagnetic amplifiers and other devices based on nonlinear effects, narrow line width and high saturation magnetization are desirable to reduce pumping power. The narrow line widths are desirable in connection with mixers and doublers, depending on second-order terms in the time varying component of the magnetization vector. This

implies the use of single crystal materials, and the inherent stability of the garnet structures would indicate greater ease in obtaining the needed higher resistivities.

Current Trends in Ferrite Applications

While the microwave properties of ferrites have been applied to a large number of useful devices, new and improved devices are vitally needed in several areas.

Considerable effort is currently being given to extending ferrite applications down to L-band and UHF. Availability of low noise microwave amplifiers has stimulated attempts to achieve lower insertion loss in conventional devices, particularly circulators. The advantages of inertialess antenna beam steering have aroused interest in the use of ferrites for rapid phase shifting or switching. Studies of high power effects indicate that ferrites may be useful for limiting, harmonic generation, and microwave delay techniques. Applications of ferrites and antiferromagnetic materials to millimeter wave devices are also being investigated.

Several requirements must be met by ferrite phase shifters before practical application of them can be made in electronically scanned antenna arrays. For a planar array, the phase shift taper across the array must be linear and must be an accurately known function of the applied signals from the scanning programmer. Also, it must be possible to change the phase taper rapidly with a minimum of driving power. Successful application of ferrite phase shifters requires materials with very little variation of saturation magnetization with temperature. The requirement for uniform behavior of all the phase shifters in the array makes it desirable to use materials whose properties are closely reproducible from batch to batch. The difficulty of achieving this in polycrystalline ferrites would make it worthwhile to consider using long single crystals in this application.

For millimeter-wave devices operating at fields below resonance, a high saturation magnetization is the main requirement. For conventional ferrites, resonance at 70 KMC would occur for a field of approximately 25,000 oersteds, requiring an extremely bulky and power consuming room temperature magnet. Super-conducting magnets (10,11) would solve these problems, but the associated cryogenic equipment might be undesirable. The high anisotropy fields in certain ferrites can be used to aid the applied field, thereby alleviating the external magnet requirements. Barium ferrite has a uniaxial field of about 1700 oersteds, which adds directly so that resonance at 70 KMC requires an additional applied field of only 8000 oersteds (12,13). Antiferromagnetic materials also have high effective internal fields. Chromic oxide and manganese fluoride appear applicable to millimeter devices, although they must be used at liquid nitrogen and helium temperatures, respectively (14).

Harmonic generation of millimeter waves has been demonstrated using single crystal YIG spheres to obtain conversion efficiencies of a few percent for doubling from 70 to 140 KMC/s with input powers of a few kilowatts (15).

In addition to the nonlinear behavior mentioned in the preceding section, other high power effects occur which have application to millimeter-wave devices. The resonance broadening and appearance of a subsidiary absorption are illustrated in figure 2. For lower frequencies, coincidence of the main and subsidiary resonance occurs and an expression for critical power (16) may be written as:

$$P_{crit} = K \frac{(\Delta H)^4}{(M_s)^2}$$

At higher frequencies, the critical power is expressed by

$$P_{crit} = K \frac{(\Delta H)^3}{M_s}$$

This means that the critical power in single crystal YIG with $M_s = 1780$ gauss and ΔH of about one oersted may be a few microwatts at frequencies below 3300 MC/s and a few milliwatts at higher frequencies. Broadening of the main resonance results in reflection limiting in a magnetic resonance filter, and the appearance of the subsidiary resonance results in absorption limiting. While restricting the power handling capability of ferrite devices, this limiting may be used to advantage for stabilizing the output level of CW sources or for preventing saturation of CW amplifiers.

This high power effect has been described previously as due to excitation of higher order spin wave modes. The spin waves are coupled to phonons (17,18). Bommel and Dransfeld (19) used this fact to make a transducer between a microwave cavity and a quartz rod for propagation of acoustic waves at microwave frequencies. Availability of long single crystals of garnets might stimulate some experiments in the use of garnets as sonic delay elements at microwave frequencies.

Progress in Materials

The past year saw the first device which uses a single crystal ferrimagnetic oxide marketed. Using a concept suggested by DeGrasse, the Watkins-Johnson Company has developed a tunable filter operating over 2 to 4 KMC which uses a single crystal YIG sphere. Using the same concept, work on ferrimagnetic limiters is being done in many laboratories. The use of single crystal ferrites of higher saturation magnetization will permit higher frequency operation of both types of devices. Lithium ferrite is now the best candidate for the latter application.

The growth of single crystals of garnets has been further perfected. From a flux, Nielsen has obtained crystals (figure 4), which weigh up to 95 g each and are 80 percent sound. Kramarsky (not published) has grown crystals of YIG with ferromagnetic resonance line widths approaching 0.2 oersteds at room temperature.

Nothing representing a notable breakthrough has occurred recently in polycrystalline ferrite compositions. Progress has mostly been in the processing techniques where efforts have been made to minimize losses and ensure uniformity and reproducibility in ferrites.

The magnitude of the low field loss due to domain wall motion can be reduced by the use of fine-grained ferrites in which the crystallite size is less than the size of a single domain. However, it is still necessary to dilute the ferrite to prevent the crystallites from interaction which will cause a considerable increase in the line width.

One very promising improvement has been reported by Malinofsky (20). He has prepared Ni ferrite by the flame spray technique and has achieved particle sizes of less than the domain size of the material. The domain rotation loss observed in most ferrites near

1000 MC was completely suppressed. This result could be important to those microwave applications where low field losses are a problem.

Although not strictly in the materials area, the observation by Hartwick, Peressini, and Weiss (21) that the subsidiary resonance in YIG crystals can be completely suppressed by modulating the dc field is extremely important. This experiment was performed to test a prediction of Suhl's (22), which promises to increase the signal level at which ferrites can be used. Weiss (23) has also suggested that the proper modulation of the dc field may lead to early appearance of subsidiary resonance. This would make very low level limiters possible.

The problems in ferrites remain much the same, that is, poor reproducibility, poor loss characteristics, etc. In addition, the increasing use of high power levels in radar systems compound these difficulties. Possibly, there are still ferrite systems and processing techniques left which will drastically improve ceramic ferrite performance, but much work has been done and the performance of most compositions can be predicted fairly well. Thus, barring discovery of a new system, the power levels above which ferrites cannot be used are probably in sight. For instance, Schlomann, et al. (24), has suggested the upper limit of peak power for resonance isolators to be several megawatts.

The problem of making low loss, low saturation, high Curie temperature ferrites for S- and L-band devices has not been completely solved although gadolinium substituted YIG has come into use more and more.

In the single crystal growth field one big problem remains—the growth of sound, large crystals of ferrites and substituted garnets which are stoichiometric and of uniform composition. In other words, the problem of the growth of large, uniformly stoichiometric crystals of high melting oxide solid solutions has not yet been solved.

Conclusion

In the light of much of the past effort in developing ferrite materials and applications, there is a point which can hardly be overemphasized. Significant advances in any of these areas require not only efforts in developing ferrites with microwave properties tailored for particular applications, but also investigations of the physical mechanisms affecting the microwave properties. Recent years have brought significant advances in ferrite theory and a greater understanding of their behavior in microwave and other applications. Much of this resulted from the observations made in carefully conducted empirical investigations. However, a tremendous amount of effort devoted to experimentation or "development of improved ferrites" has been of dubious, if any, value. For example, some extensive programs were launched to establish quantitative correlation between processing parameters of some low loss ferrites before properly determining that a specific single phase material actually contained an extremely "lossy" second phase.

Recommendations

Some considerations for future effort in the area of ferrite materials are:

1. The effect of materials purity as well as oxygen stoichiometry on conductive behavior. This would involve a rather detailed treatment of conduction processes and a definition of constitutional diagrams to differentiate between single phase and "spinel-plus" compositions.

2. Preparation and study of single crystals in representative ferrite classes and serious attempts to bring polycrystalline properties nearer to those of the single crystal. Rupprecht (not published) has shown that losses in the ceramic form of SrTiO_3 dielectrics can be brought to within a factor of twice the single crystal properties by control of purity and post-sintering anneals.

3. Survey of ferrite properties over respectable temperature and frequency spectra. As indicated by some of the considerations in this discussion, a spot check of ferrite properties at a single frequency well below the intended frequency may be hopelessly inadequate in many cases. This may explain why published literature on microwave ferrites with property data of only 20 MC is so discouraging. Goodwin (not published) has conducted extensive measurements on a number of commercial ferrites and garnets at 77°K and at 4.2°K.

4. A first look at thiospinels or ferrites based on other unusual spinel systems.

5. Consideration of topotactical grain orientation, magnetic anneal, or other means for achieving orientation in ferrites for specific purposes.

REFERENCES

1. Pringle, D.H., and Hepburn, W.D., "Solid State Phys. in Elect. and Telecom," Proc. of Int. Un. of Pure and Appl. Phys., Vol. 3, Pt. I, Brussels, 1958.
2. Dr. Davis, Raytheon. Private communication.
3. Polder, D., and Smit, J., Rev. Mod. Phys., Vol. 25, 89, 1953.
4. Rado, G.T., Wright, R.W., and Emerson, W.H., Phys. Rev., Vol. 80, 273, 1950.
5. Snoek, J.L., Physica's Grav., Vol. 14, 207, 1948.
6. Wijn, H.P.J., Gevers, M., and Van der Burgt, C.M., Rev. Mod. Phys., Vol. 25, 91, 1953.
7. Whitehead, C.W., and Wills, M.S., Admiralty Internal Report. July 1957.
8. Lax, B., Proc. Inst. Radio Engrs., N.Y., Vol. 44, 1368, 1956.
9. Suhl, H., Phys. Rev., Vol. 106, 384, 1957.
10. Kunzler, J.E., Buehler, E., Hsu, F.S.L., and Wernick, J.H., "Superconductivity in Nb_3Sn at High Current Density in a Magnetic Field of 88 K Gauss," Phys. Rev. Letters, Vol. 6, 89, 1961.
11. Arp, V.D., Kropschot, R.H., Wilson, J.H., Love, W.F., and Phelan, R., "Superconductivity of Nb_3Sn in Pulsed Fields of 185 Kilogauss," Phys. Rev. Letters, Vol. 6, 452, 1961.
12. Brady, I., and Collins, T., "Ferromagnetic Line Width of Single Crystals of Barium Ferrite," Tech. Rept. 2116, DA Task Nr 3A99-15-001-01, U.S. Army Signal Research and Development Laboratory, Ft. Monmouth, N.J., 1960.

13. DeBitetto, D.J., du Pre, F.K., Brockman, F.G., Steneck, W.G., Jr., "Hexagonal Magnetic Materials for Microwave Applications," Third Quarterly Report, Contract Nr DA 36-039-SC-85279, Philips Laboratories, Irvington-on-Hudson, N.Y., 1960.
14. Heller, G.S., Stickler, J.J., and Thaxter, J.B., "Antiferromagnetic Materials for Millimeter and Submillimeter Devices," Report Nr 82-G-0023, AF 19(604)-7400, MIT Lincoln Laboratory, 1960.
15. "Investigation of Microwave Nonlinear Effects Utilizing Ferromagnetic Materials," 13th Quarterly Report, Contract DA 36-039-SC-73278, Melabs, Palo Alto, California, 1960.
16. Suhl, H., "The Nonlinear Behavior of Ferrites at High Microwave Signal Levels," Proc. IRE, Vol. 44, 1270, 1956.
17. Schlomann, E., "Generation of Phonons in High-Power Ferromagnetic Resonance Experiments," J. Appl. Phys., Vol. 31, 1647, 1960.
18. Turner, E.H., "Interaction of Phonons and Spin Waves in Yttrium Iron Garnet," Phys. Rev. Letters, Vol. 5, 100, 1960.
19. Bommel, H., and Dransfeld, K., "Excitation of Hypersonic Waves by Ferromagnetic Resonance," Phys. Rev. Letters, Vol. 3, 83, 1959.
20. Malinofsky, W.W., Babbitt, R.W., J. App. Phys. Supplement, Vol. 32, Nr 3, 2375, 1961.
21. Hartwick, T.S., Peressini, E.R., and Weiss, M.T., Phys. Rev. Letters, Vol. 6, 176, 1961.
22. Suhl, H., Phys. Rev. Letters, Vol. 174, 1961.
23. Weiss, M.T. Paper presented at a conference on ferromagnetics and ferroelectrics, California Inst. of Tech., 23 February 1961.
24. Schlomann, S., Saunders, J.H., and Sirvetz, M.H., IRE Trans. on Microwave Tech., Vol. 8, Nr 1, 96, 1960.

TABLE I
MICROWAVE FERRITE APPLICATIONS

FARADAY ROTATION	PHASE SHIFT	RESONANCE ABSORPTION	SECOND-ORDER EFFECTS	NON-UNIFORM SPIN WAVE MODES
Switch Circulator	Gyrator	Resonance Isolator	Frequency Doubler	Ferromagnetic Amplifier
45-Degree Rotational Isolator	Field Dis- placement Isolator	Circular Polarizer	Mixer Detector	Limiter
Amplitude Modulator	Frequency Modulator			

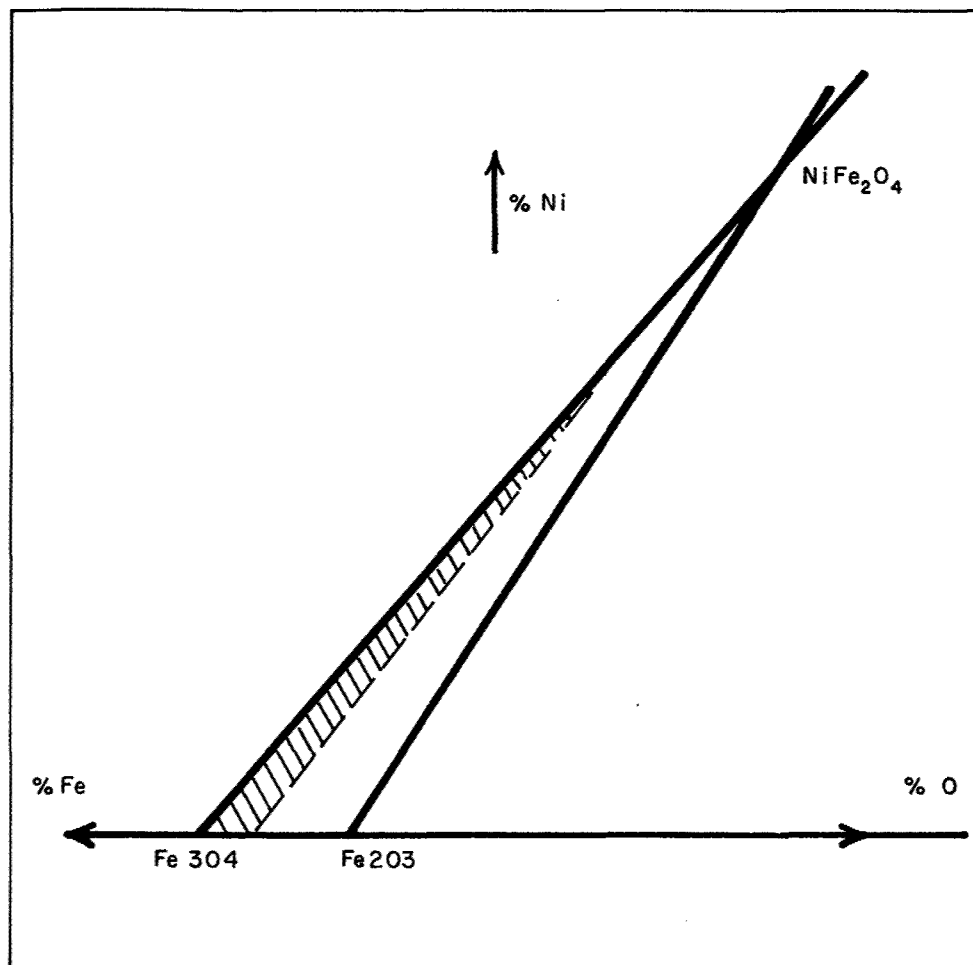


Figure 1. Monophase Spinel Region for Ni Ferrite

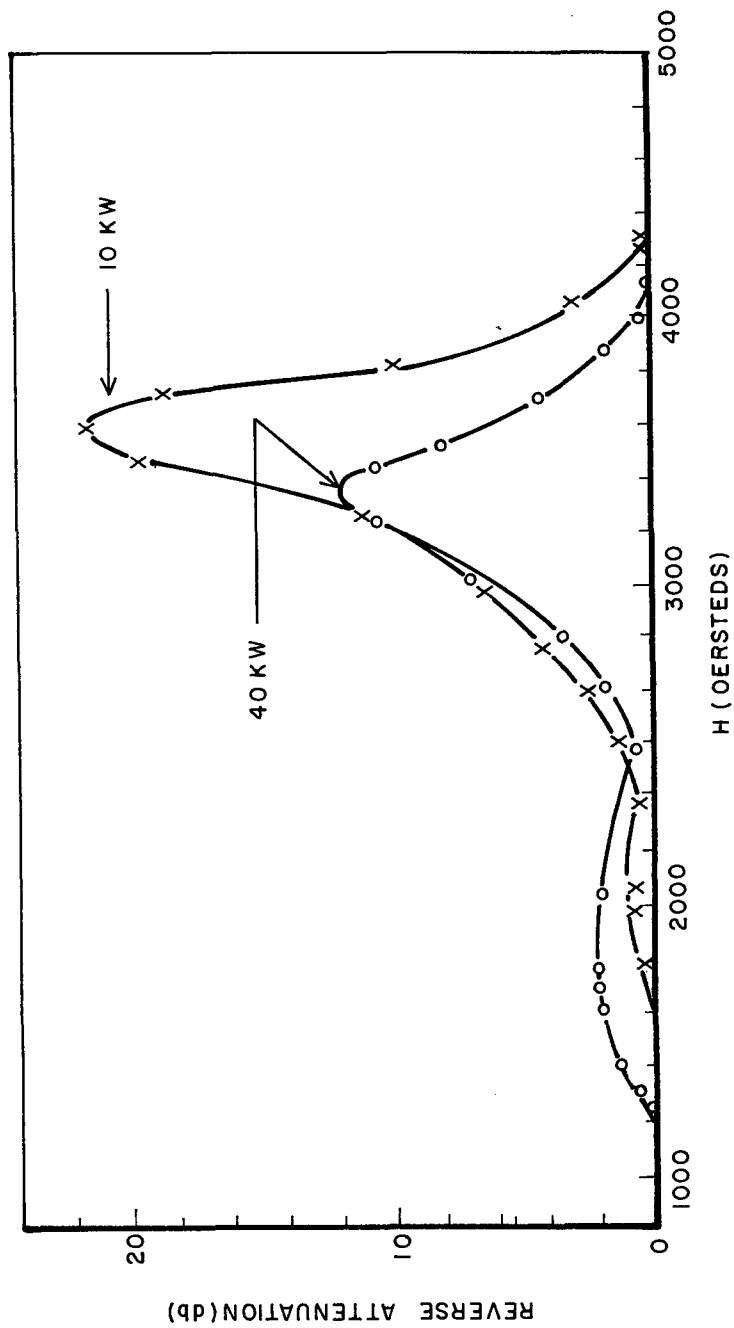


Figure 2. Effect of Power Level on Resonance Absorption of a Mg-Mn Ferrite

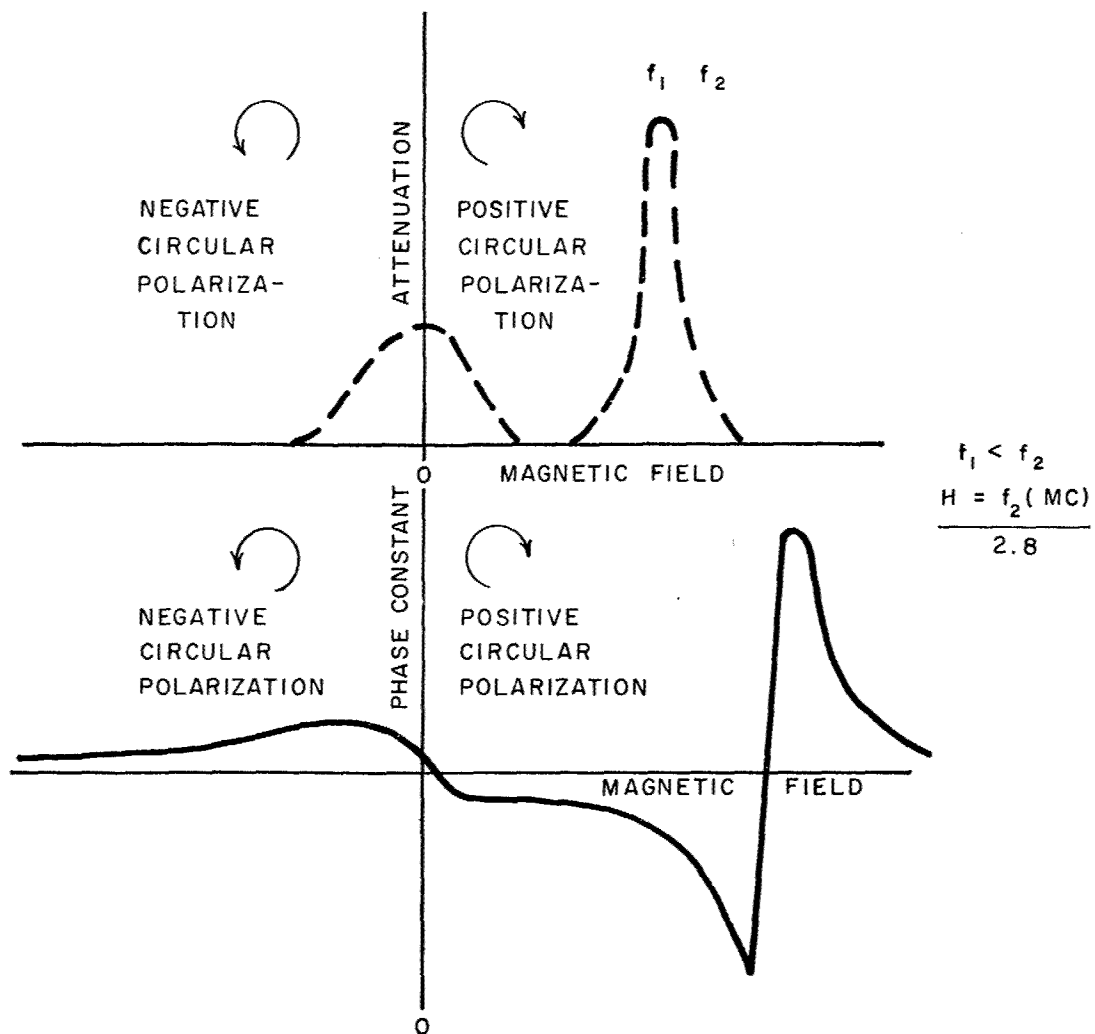


Figure 3. Typical Phase and Attenuation Characteristics Vs Applied Field



Figure 4. Single Crystals of Garnets

HARD MAGNETIC MATERIALS

Dr. Karl Strnat

Directorate of Materials and Processes, ASD

Introduction

Permanent magnets are vital parts of a great variety of electrical and electronic equipment used by the Air Force, aloft or on the ground. Hundreds of magnets are used in a modern plane or missile, in communication and navigation equipment, in small motors and generators, in many measuring instruments, etc. The following is a selection of important Air Force applications of permanent magnets:

- Moving coil instruments
- Motors, generators (stator field)
- Combustion engine ignition (magnets)
- Relays
- High frequency tubes (magnetron, traveling wave tube)
- Load isolators
- Biasing of ferrite cores
- Loud speakers
- Telephone receivers
- Cathode ray tube biasing
- Magnetostrictive devices (Sonar)
- Magnetic drives
- Magneto-hydrodynamic boundary layer control (nose cones)

If we consider their diversified functions, it becomes obvious that there is not one "best magnet material" but that quite different qualities are expected of magnets for various uses. An instrument magnet, for instance, must be highly insensitive to demagnetizing fields, temperature independent near room temperature, and not subject to aging. High power tube magnets have to operate at elevated temperatures and must produce high flux. Biasing magnets for ferrite cores must be electrical insulators. Magnets for speakers, motors and generators should have primarily high energy products, etc. Weight will be a prime consideration in airborne equipment; and low price non-strategic materials will further qualify a magnet where large quantities are required.

These rather stringent requirements justify the considerable effort being expended both here and abroad to create improved permanent magnets. Noteworthy is the Air Force sponsorship, which has for years stimulated the permanent magnet research in American industry.

For a long time, permanent magnets were made of hardened steels, had low energy products, and unsatisfactory coercive forces. With the discovery of the first precipitating alloys of the Alnico-type in 1931 a rapid development of magnetic materials began which has not lost momentum. In recent years, better theoretical understanding has brought about the concept of fine particle magnets, which hold great promise for the future. The trend of the maximum energy products obtained in laboratory sample, shown in figure 1, illustrates these impressive achievements.

The Physical concepts of Permanent Magnets

In simple terms, the main purpose of a permanent magnet is to produce a magnetic flux as large as possible between its pole faces without the necessity for maintaining an exciting field. To best achieve this purpose, we need a material with a high saturation magnetization; we want to preserve a large fraction of the saturation, preferably 100 percent, as remanence when the magnetizing field is removed; and we want to protect this remanence against the adverse influence of demagnetizing fields (in other words, we need a high coercive force). Figure 2 is intended to recall some of the terms used in the description of permanent magnets.

The criterion "high saturation" serves mostly to pre-select potential magnet materials and is not too restrictive. There is little hope that materials can be tailor-made with saturation values significantly higher than those known. For a given basic material, however, we can do much about the other two factors, remanence and coercive force, by modifying the structure of the materials.

Magnetization reversal can basically happen by two processes: domain wall motion and rotation of all spins more or less simultaneously (figure 3). The first of these processes is the dominating one in all soft magnetic materials and also in the conventional permanent magnets.

The motion of domain walls requires only a little energy and thus yields a low coercive force. One way magnetically to harden magnet materials is to impede the wall motion by creating obstacles. This can be done by inducing random strains by strong deformation or thermal quenching or by precipitating non-magnetic inclusions. Magnet materials of this type range from simple martensitic carbon steels, which are now rarely used, through alloyed steels containing cobalt, chromium, tungsten, manganese and/or molybdenum, to alloys such as Cunife, Cunico, Vicalloy, and others in which iron is no longer the main constituent. The best magnetic properties achieved with steels were, perhaps, $B_H C$ 250 oersted and $(BH)_{\max} = 1 \times 10^6$ gauss-oersted, while the limits of alloys hardened by non-magnetic precipitates are nearer $H_c = 800$ oersted and $(BH)_{\max} = 2 \times 10^6$ gauss-oersted. Some of these alloys are strongly anisotropic as a consequence of cold-rolling or drawing.

The second basic mechanism of magnetization change, simultaneous rotation of all spins in a domain, requires much higher energies than the shifting of domain walls. It is the process by which saturation is approached in an isotropic, polycrystalline

ferromagnetic material at high field strengths and long after all wall motions have been completed. This suggests that, by eliminating all domain walls and relying solely on rotations, we could make a material in which the magnetization reversal would require very high fields--one of the fundamental properties a permanent magnet must have.

This concept (that the coercive force of a ferromagnetic powder aggregate increases with decreasing size of the particles which form the powder) is the basis for the modern fine particle magnets (figure 4). It was first noted by Gottschalk and since confirmed by many other workers on a variety of materials. This phenomenon is ascribed to the approach to a "single domain" particle behavior. When the particle diameter becomes comparable to the thickness of a Bloch wall, the formation of such a wall becomes energetically less favorable than the magnetization reversal by spin rotation; and, the particle tends always to remain one single magnetic domain. The coercive force which can be obtained with such powder magnets depends on the strength of the forces which bind the magnetization vector to certain favored directions within the particles. The origin of these forces can be the so-called crystal anisotropy in which the magnetization lies preferentially in certain directions of the crystal lattice or the shape anisotropy for which the long axis is a magnetic preference direction in an elongated particle. Fine particle magnets based on either of these types of anisotropy have been produced. Two other possible ways to create a magnetic preference direction in particles by straining a highly magnetostrictive precipitate or by making use of the so-called exchange forces between the particle and on anti-ferromagnetic shell are being studied in different laboratories but have not yet been used for commercial magnets. To reach the highest possible remanence with any fine particle magnet, however, it is necessary to align the particles with their easy axes parallel to one another.

The best properties so far obtained for powder magnets in laboratory experiments are $B_r = 4,800$ gauss, $M^H_C = 3,650$ oersted, $(BH)_{\max} = 5.4 \times 10^6$ gauss-oersted for manganese-bismuth (a material of no practical importance so far) and $B_r = 10,800$ gauss $H_c = 950$ $(BH)_{\max} = 6.5 \times 10^6$ gauss-oersted for elongated iron-cobalt particle magnets. The theoretical limits lie much higher, for elongated iron-cobalt particle magnets, for instance, at $B_r = 16,300$ gauss $H_c = 4,100$ oersted and $(BH)_{\max} = 50 \times 10^6$ gauss-oersted (4).

The highest energy products of all magnets where $(BH)_{\max} = 12 \times 10^6$ gauss-oersted combined with $H_c = 1,300$ oersted and $B_r = 12,000$ gauss in the best laboratory samples, are obtained with alloys of the Alnico type. Their properties are determined by highly ferromagnetic precipitate in a weakly ferromagnetic matrix which exhibits also near single domain behavior. The structure is quite complicated, however, and not yet fully understood although much progress in this respect has been made in the last few years (8, 9). These alloys can be cast or sintered and a preferred orientation can be created by a proper field anneal. While they have excellent magnetic properties, Alnico magnets are expensive and contain large amounts of Co and Ni, materials of limited supply. This is true also for the ferrous-cobalt particle magnets (but not for some of the other powder magnets including those of iron), provided the matrix problem can be solved satisfactorily.

The non-metallic ferrite magnets, of which only barium ferrite and, to a lesser degree, cobalt ferrite have technical importance, also owe their high coercive force to a fine subdivision of the material with high crystal anisotropy. However, they do not consist of genuine single-domain particles and domain walls do exist in them. The best reported values for ferrite magnets are $B_r = 4,000$ gauss, $H_c = 2,000$ oersted $H(BH)_{\max} = 3.7 \times 10^6$ gauss-oersted. Barium ferrite, being made of inexpensive and non-critical raw materials, is today the most-used permanent magnet material in western Europe and in Russia, and will undoubtedly find an expanding market in this country as well.

Summary and Outlook

In figure 5, typical demagnetization curves are shown for most of the materials previously discussed. They are representative of what is at present commercially available.

If we try to envision the future development of permanent magnet materials, we can safely assume that the efforts will concentrate on single domain particle magnets in the wider sense. Of these the properties of barium ferrite are rather near their theoretical upper limits now and only incremental improvements can be expected here. Other ferrite compositions with higher saturation magnetization may be formed, however, and ferrites with higher Curie temperatures would be especially valuable for many Air Force uses which call for elevated operating temperatures.

Considerable improvement can still be expected of the Alnico materials; continuation of the research efforts to understand their precipitation mechanisms, their structure and its relation to the magnetic properties are pre-requisites for systematic material development. Air Force sponsored studies of the high temperature properties of a variety of permanent magnets have proved Alnico V and VI useful for application at operating temperatures above 500°C (10). Such investigations will also have to be continued and extended to materials not heretofore tested.

Elongated particle magnets need considerable improvement. New matrix materials, in addition to lead and plastics, should be found for the iron and iron-cobalt magnets, and methods devised for producing more uniform, near-cylindrical particles to permit a further increase of the maximum energy product.

Attempts should also be made to produce elongated particles of other materials, possibly combining the action of crystal and shape anisotropy by making single crystal particles whose long axis will coincide with a direction of minimal magneto-crystalline energy. A recent publication reported that it is also possible to produce oxide-covered particles which derive their coercive force from the shell while the metal core provides the remanence.

For fine particle magnets based on crystal anisotropy, manganese-aluminum is a material most worthy of intensive study (11). Investigation of other known or heretofore not produced magnetic intermetallic compounds may well bring about new promising materials with high crystal anisotropy, sufficiently high saturation and Curie point, and good environmental stability.

Finally, pursuit of the concept of exchange coupling between an antiferromagnetic layer and a ferromagnetic particle of film may eventually lead to the development of practical magnets of unidirectional behavior (ref. 12).

BIBLIOGRAPHY

1. Sixtus, K.J., "A Study of Permanent Magnets of the Barium Ferrite Type" WADC TR 56-198, ASTIA Doc. No. AD 110551.
2. Kronenber, K.J. and Tenzer, R.K., "A New Approach to Analyzing the Phases of Alnico V", ASTIA Doc. No. AD 203383.
3. Alberts, P.A. and Carr, W.J., J. Appl. Phys. 32 (1961), 2015.
4. Luborsky, F.E., J. Appl. Phys. 32 (1961), 1715.
5. Gottschalk, V.H., Physics 6 (1935), 127.
6. Polgreen, G.R., Iron Steel Inst., Special Report No. 58 (1954), 24.
7. Falk, R.B. and Hooper, G.D., J. Appl. Phys. 32 (1961), 1905.
8. Kronenber, K.J., J. Appl. Phys. 32 (1961), 1965.
9. Campbell, R.B., and Julien, C.A., J. Appl. Phys. 32 (1961), 1925.
10. Tenzer, R.K., "The Remanence of Alnico V and VI Between Room Temperature and 550°C", WADD TR 59-438.
11. Koch, A.J. et. al., J. Appl. Phys. 31 (1960), 75S.
12. Meiklejohn, W.H. and Bean, C.P., Phys. Rev. 102 (1956), 1413.

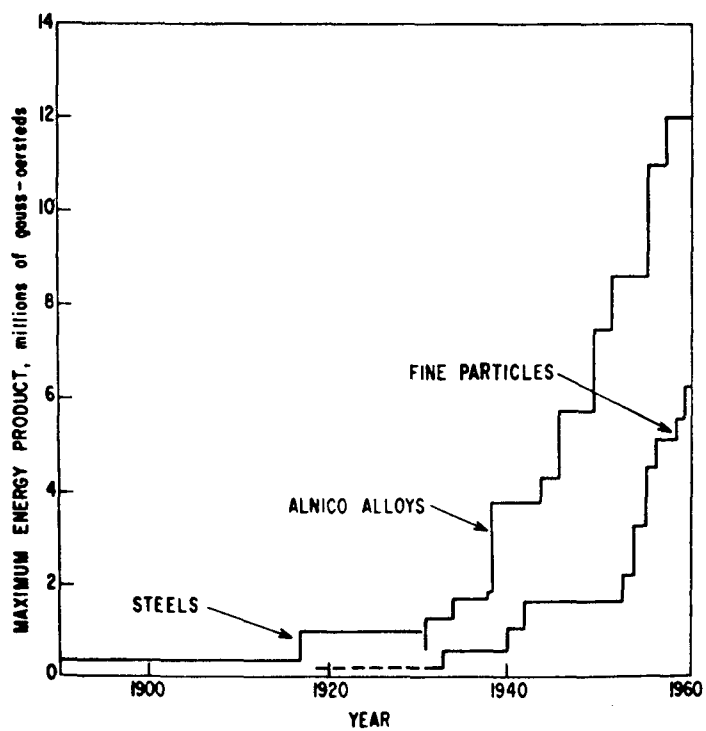


Figure 1. Progress in Permanent Magnet Development (From Ref. 4)

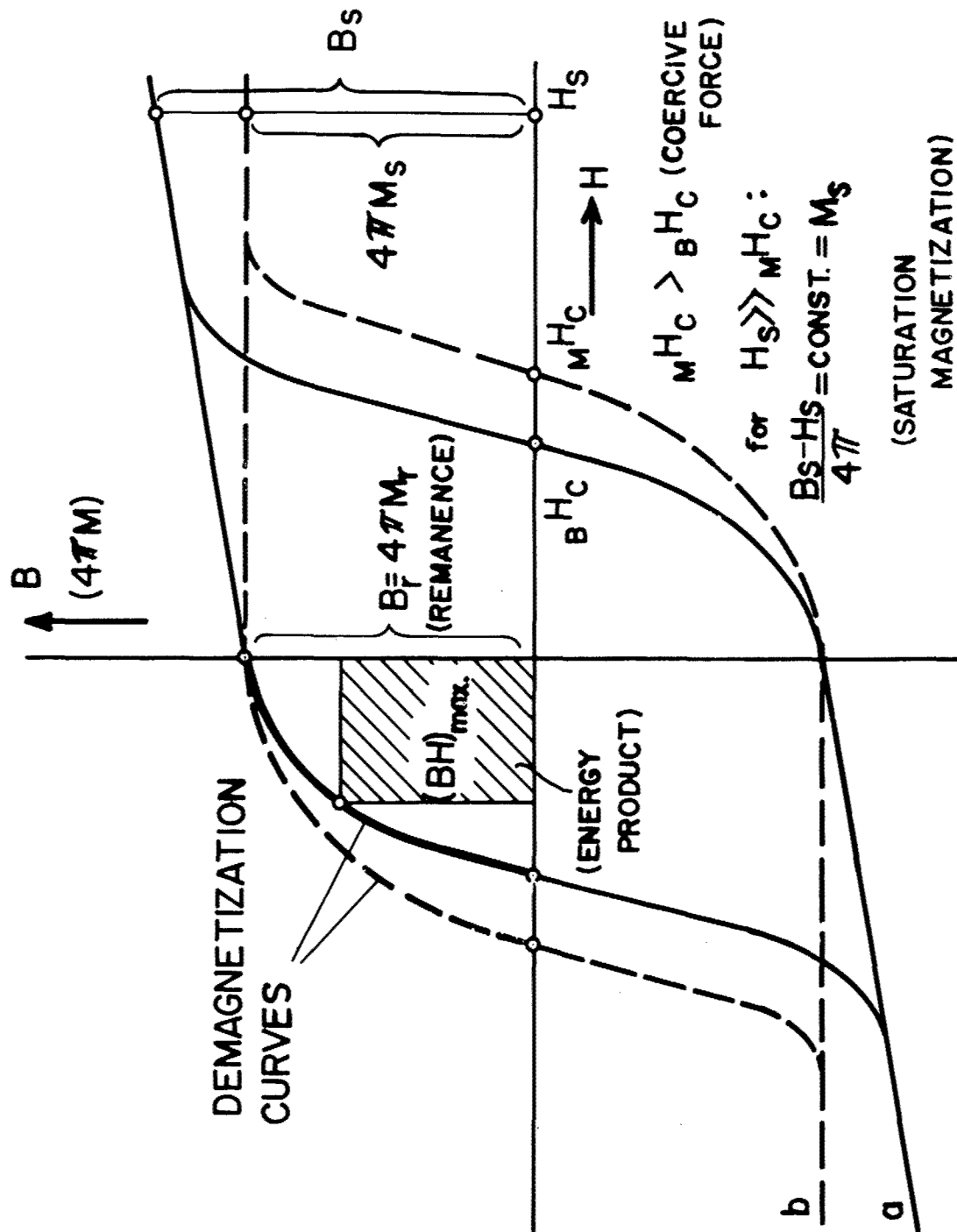
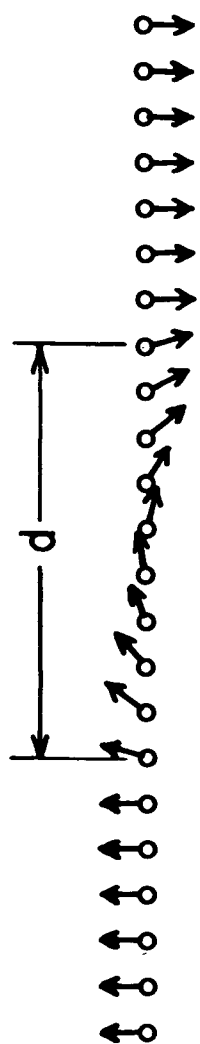
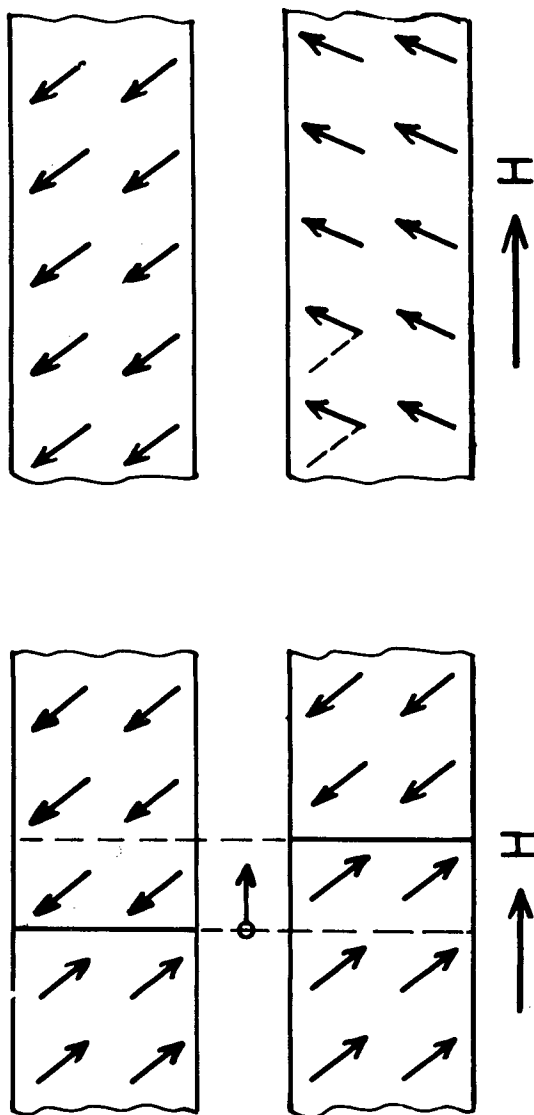


Figure 2. Terms Used in the Description of Permanent Magnets



SPINS IN A DOMAIN WALL



(a) DOMAIN WALL MOTION (b) UNIFORM SPIN ROTATION

Figure 3. Processes of Magnetization Reversal

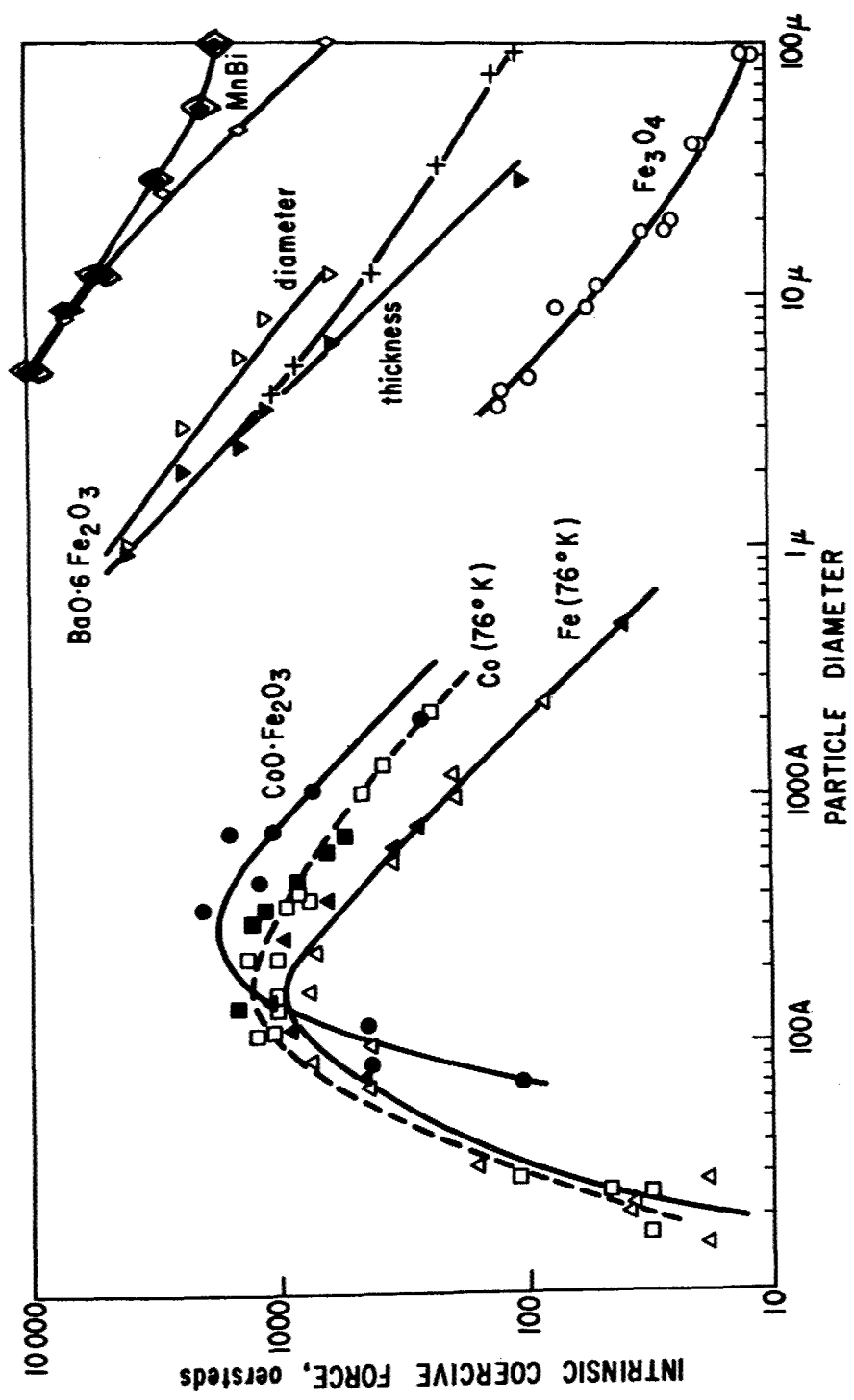


Figure 4. Relation Between Coercive Force and Diameter of Fine Particles with High Crystal Anisotropy (From Ref. 4)

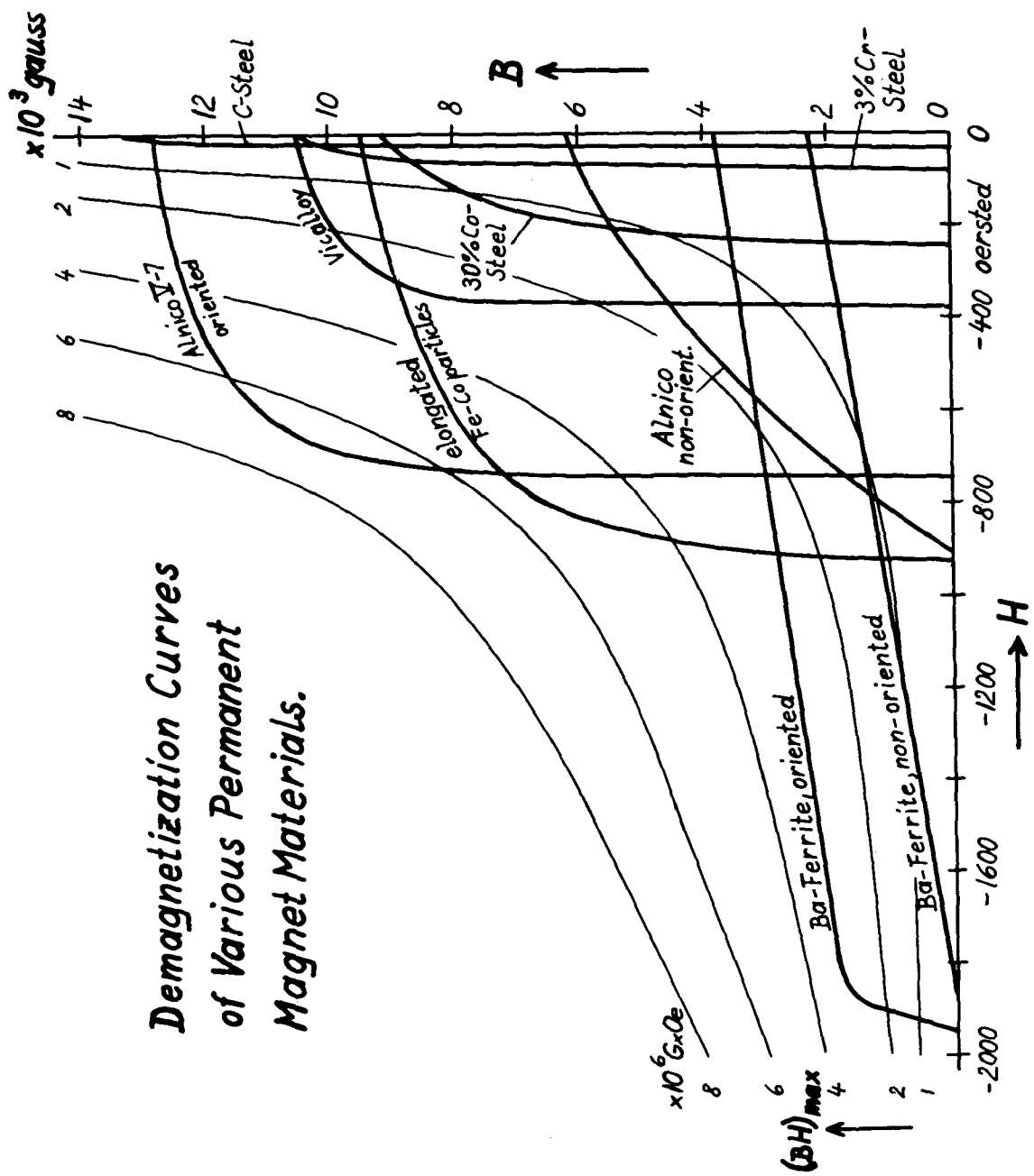


Figure 5. Demagnetization Curves of a Representative Selection of Commercially Available Magnet Materials

SOFT MAGNETIC METALLIC MATERIALS

John C. Olson

Directorate of Materials and Processes, ASD

Introduction

Good magnetically soft metallic materials are characterized by low hysteresis losses, low eddy current losses, high magnetic permeability, high saturation values, and either a minimum or a decided change in permeability with temperature.

Air Force applications of these materials are dictated by the attainment of these properties in concert with minimum weight, size, and cost. Air Force requirements for soft magnetic metallic materials encompass their usage in transformers, for power and audio frequencies; controls, such as motors and relays; magnetic amplifiers; and thin films with very fast switching times for computers. Many of these applications will require the ability to withstand hyper-environments, due to hypervelocity vehicles and space flights. Normal operations in the future may infer sustained high temperatures or nuclear radiation or both. The principle radiation hazard will consist of fast neutrons. The thermal environment is much harder to predict. High temperatures are well-known to be deleterious to soft magnetic materials and the effects of nuclear radiation have not yet been thoroughly studied. For devices which must operate during re-entry the temperatures encountered exceed even 1000°C at some points in the vehicle.

In spite of these adverse conditions, however, magnetic materials will still play an important part in the space flight age. The properties of soft magnetic materials today, as outlined above, have developed only through investigations of the basic mechanism requirements. There is now and will continue to be a need for additional basic research of this kind as well as an extensive search for new materials to meet the increasingly difficult requirements being encountered as a result of the extreme temperature and radiation environments imposed by aerospace operations.

Factors Affecting Magnetic Properties

Magnetic properties, or more specifically, ferromagnetic properties, are highly dependent upon chemical composition and crystal structure. The phenomena of ferromagnetism results when a paramagnetic material possesses a spontaneous magnetic moment. (Although individual atoms of paramagnetic materials exhibit magnetic moments because of their unpaired electron spins, they are so randomly oriented that no net moment can be observed in volumes as small as a few lattice constants of the material.) Ferromagnetism is a crystal property and results from the parallel alignment of the individual magnetic moments because of favorable interactions between paramagnetic atoms and their neighbors within the crystal lattice. As shown in figure 1 these individual magnetic moments tend toward parallel alignment with increasing strength as the separation between nuclei becomes optimum. This desirable condition reaches its maximum with the transition metals, iron, cobalt, and nickel. Crystals of these rare earth elements are ferromagnetic only near absolute zero. Where the nuclei are too close together the forces align moments anti-parallel and the substances have no net moment; however, the non-magnetic elements, chromium and manganese, can be made ferromagnetic by increasing their interatomic distances in the lattice structure by alloying (i.e., there are many alloys of manganese which are ferromagnetic). When the disorientation effects of thermal

vibrations overcomes the orientation effect of these alignment forces, the substance becomes non-ferromagnetic. Table 1 gives the Curie temperatures of the various ferromagnetic elements.

Magnetic properties are also very sensitive to impurities which tend to occupy interstitial spaces in the lattice and impede the easy formation of magnetic domains, thereby increasing the coercive force and hysteresis losses. But, on occasion "impurities" are deliberately added to improve other properties, such as the addition of vanadium to improve the workability of "Permendur." Usually "impurities" are added to suppress the eddy current losses by raising the resistivity of the bulk material. Iron normally has up to 4 percent silicon added to it or is alloyed with aluminum to achieve this result. Iron very often is alloyed with other metals to attain desirable effects such as higher permeability with nickel or higher saturation with cobalt.

Large grain size, or rather the exclusion of grain boundaries, is important for better magnetic properties. Since almost all ferromagnetic materials are anisotropic, grain orientation is fundamental in controlling magnetic properties. The preferential crystal directions for easy magnetization are well-known for iron and nickel and are utilized to attain higher efficiency in transformers of all types.

Heat treatment can also influence the magnetic properties of materials. In fabrication, annealing is employed to remove stresses induced which would otherwise raise the coercive force and hysteresis losses. Yet, some iron-nickel alloys which have been drastically cold rolled are under-annealed to produce a partially strained alloy with almost constant permeability.

The usual method of fabricating magnetic cores is to cast the metal and then subsequently hot or cold roll it or machine and anneal it. In some instances, the material is ground to a powder, compacted to the shape desired, and sintered. This procedure usually saves much of the production cost, but a disadvantage is a considerable loss in the magnetic properties as a natural result of the application of high temperatures. Temperature compensation may be achieved with powdered cores, however, by using two materials with opposite temperature coefficients in the desired range.

Specific Metal Core Materials

The silicon steels have gained universal acceptance in most low frequency transformer applications. The best magnetic properties are achieved by cold reduction and heat treatment techniques which produce good grain orientation; silicon steels can be heat treated so that they will not age significantly. The silicon content of the best materials is from 3 percent to 3.5 percent.

The reaction of aluminum to electrical resistivity and other magnetic properties is similar to that of silicon when alloyed with iron. Until recently, however, difficulty of fabrication has suppressed the use of aluminum-iron alloys.

The nickel-iron alloy system produces ferromagnetic material at nearly all ratios of composition. The maximum saturation values are obtained at about 50/50. The highest permeabilities are found at about 78 percent Ni (i.e., Permalloy). Other elements are often added to these alloys to accentuate desired characteristics for particular applications. Figure 2 shows the dc magnetization curves for several common magnetic core materials.

The iron-cobalt alloys attain the highest saturation values of all common core materials, to wit 24,200 gauss. The inherent brittleness and low resistivity of iron alloys with greater than 30 percent cobalt, however, limits their application. But, a 2-percent vanadium addition makes the 50/50 iron-cobalt alloy workable and still maintains its very high saturation value. These alloys are of special interest to the Air Force because of their possibilities for higher temperature applications if the air oxidation problems can be solved.

Thin films of soft magnetic materials have gained increased emphasis, and much of the basic knowledge of magnetism in recent years has resulted from these studies. Thin films of nickel-iron have been produced which have nearly square hysteresis loops and magnetization cycling times of less than 0.2 seconds (3). They are particularly applicable for use in high speed computer devices; and, for thin film memory devices, cycling times in the nanosecond range can be expected if proper control of the magnetic parameters can be achieved.

Effects of Hyperenvironments

Some preliminary experimental work has been done to determine the effects of neutron irradiation and high temperature on soft magnetic materials (4). The results indicate that the softest magnetic materials are the most drastically degraded under these conditions. Neutron irradiation introduces imperfections in the crystal lattice which increases the coercive force. This explains the fact that the softest materials, having lowest coercivity because of minimum imperfections, are most radically changed by irradiation. Figure 3 shows the magnetic saturation as a function of long time exposure to an integrated neutron flux.

The "structure-insensitive" properties are generally unaffected by neutron irradiation. Core materials with coercive forces greater than 0.5 oersted are essentially undamaged by this irradiation, however these materials have initial and maximum permeabilities lower than the softer materials thereby making them less useful for many applications. Figures 4, 5, and 6 show the effect of irradiation on the coercive force and the initial and maximum permeabilities of several common core materials. Other investigators have found that the irradiation of nickel-iron alloys in the presence of a magnetic field produces a square hysteresis loop and increases residual induction but also increases the coercive force (5). Metal powders are affected less by irradiation than metal sheets and tapes because of stress relief effects, and the greatest changes are increases in the high frequency losses.

High temperature environments are also a serious problem area. Oxidation has a very deleterious effect on iron-cobalt alloys (6). However, if neutral atmospheres are employed these same materials are stable to as high as 600°C. A great many materials are limited to lower temperature applications because their Curie points are too low. Silicon-steels, for example, with Curie temperature above 700°C, have already decreased up to 20 percent in saturation induction at 500°C, and nickel-iron alloys are already at their Curie point at about 450°C.

Thermal cycling can produce irreversible changes in the magnetic properties of many core materials. Figure 7 shows the effect of such cycling on Supermendur, and figure 8 illustrates the relative insensitivity of 50/50 nickel-iron to thermal cycling. Grain-oriented materials show pronounced effects of high temperature degradation just as one should expect.

Conclusions

Although the progress of soft magnetic metallic materials has been rapid, as in many other materials, change in concept of recent years has caused change in direction of research for the future.

Immediate applications require the ability to withstand hyper-environments and require, specifically, investigations on the following subjects:

(1) Development of magnetic materials with higher Curie points. Thermal gradient can be achieved only by displacement or by some bulk thermal insulating material, either of which may not be tolerable.

(2) Research into the basic relationships between magnetic properties and atomic structures. This is necessary to develop materials for more reliable performance and greater environmental stability. Thin film investigations have done much to explain anisotropy and domain formation and should constitute a large part of this research.

(3) Development of corrosion resistant materials. This may be accomplished by more fully understanding the effects of corrosion on materials having magnetic properties.

(4) Reduced nuclear radiation effects on magnetic materials. Attention should be directed to the possible use of heavy elements (i.e., rare earth or low cross-section materials). A means to manipulate the crystal structures of the rare earth elements may result in materials with ferromagnetic properties more interesting than any materials now in existence.

(5) Finally, a re-evaluation of conventional materials is in order to determine what present materials can meet the foregoing requirements and in what areas new materials with enhanced properties must be sought.

BIBLIOGRAPHY

1. Finkelberg, W., Atomic Physics, McGraw Hill, 1950.
2. Metals Handbook, 8th Edition Vol. 1, pp 785-797, A.S.M., 1961.
3. Bittmann, E.E., "Designing Thin Film Memories For High Speed Computers," Electronics, 39, March 1961.
4. Gordon, D.I., "Magnetic Cores and Permanent Magnets in Hyper-Environments," U.S. Naval Ordnance Laboratory, Silver Springs, Md, 1960.
5. Schindler, A.I., and Salkovitz, E.I., "Effect of Applying a Magnetic Field During Neutron Irradiation on the Properties of Fe-Ni Alloys," Journal of Applied Physics, Vol 31 Supp to No. 5, 245-5, 1960.
6. Pavlik, N., "High Temperature Stability of Magnetic Materials," Journal of Applied Physics, Vol 32 Supp to No. 3, 1961.

Table 1
FERROMAGNETIC ELEMENTS & THEIR CURIE TEMPERATURES

ELEMENT	CURIE POINT
Iron	770°C
Cobalt	1127°C
Nickel	358°C
Gadolinium	16°C
Dysprosium	178°C

MAGNETIC BEHAVIOR AS A FUNCTION OF ATOMIC & CRYSTAL STRUCTURE

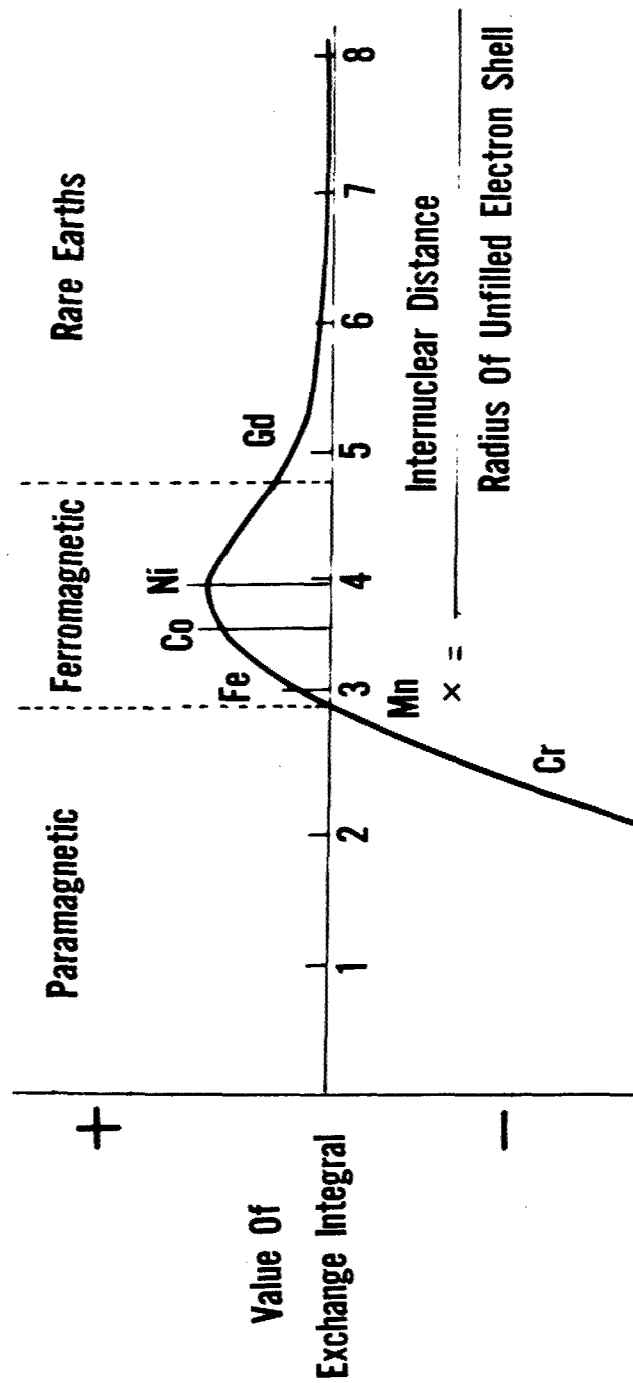


Figure 1.

D.C. MAGNETIZATION CURVES OF VARIOUS MATERIALS

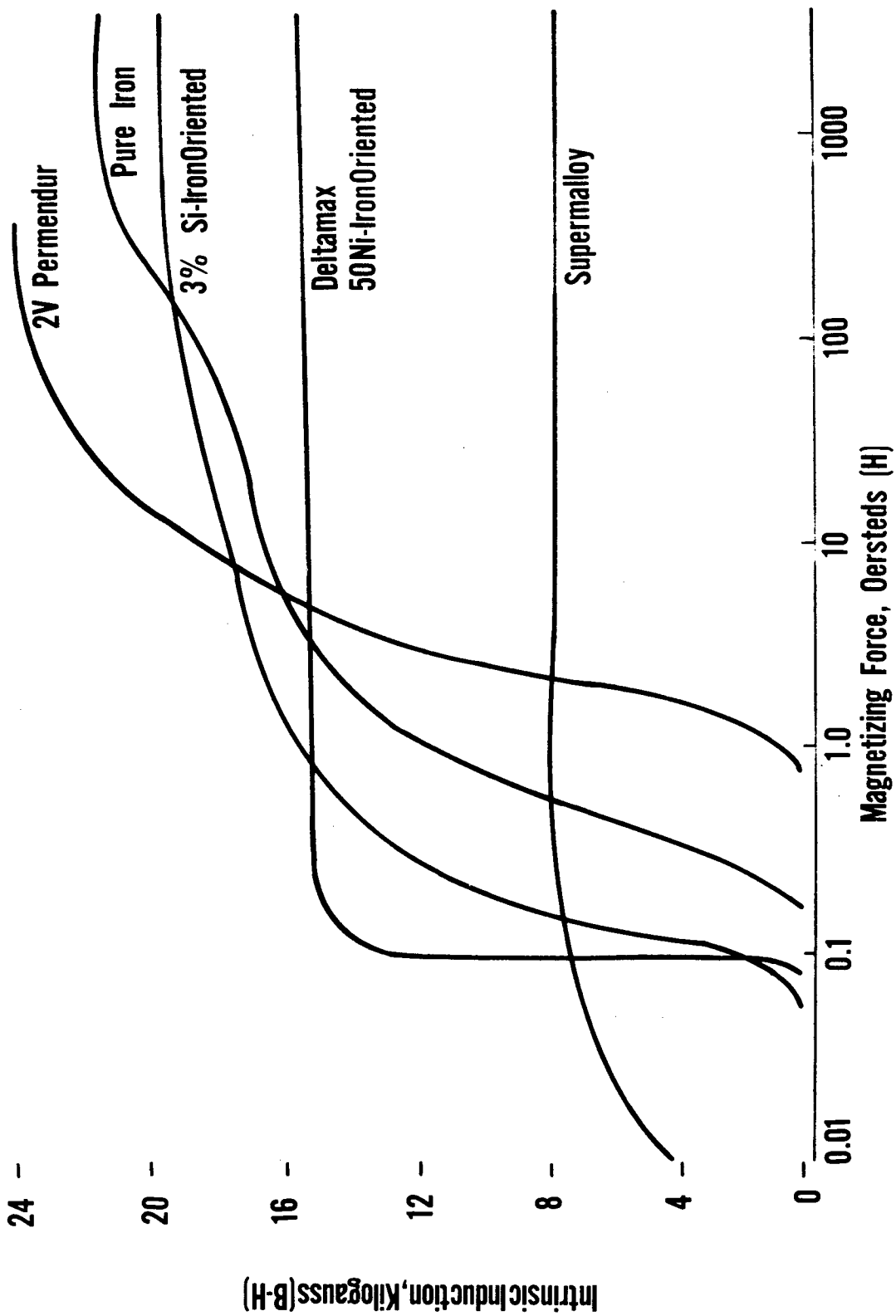


Figure 2.

EFFECT OF RADIATION ON MAGNETIC SATURATION

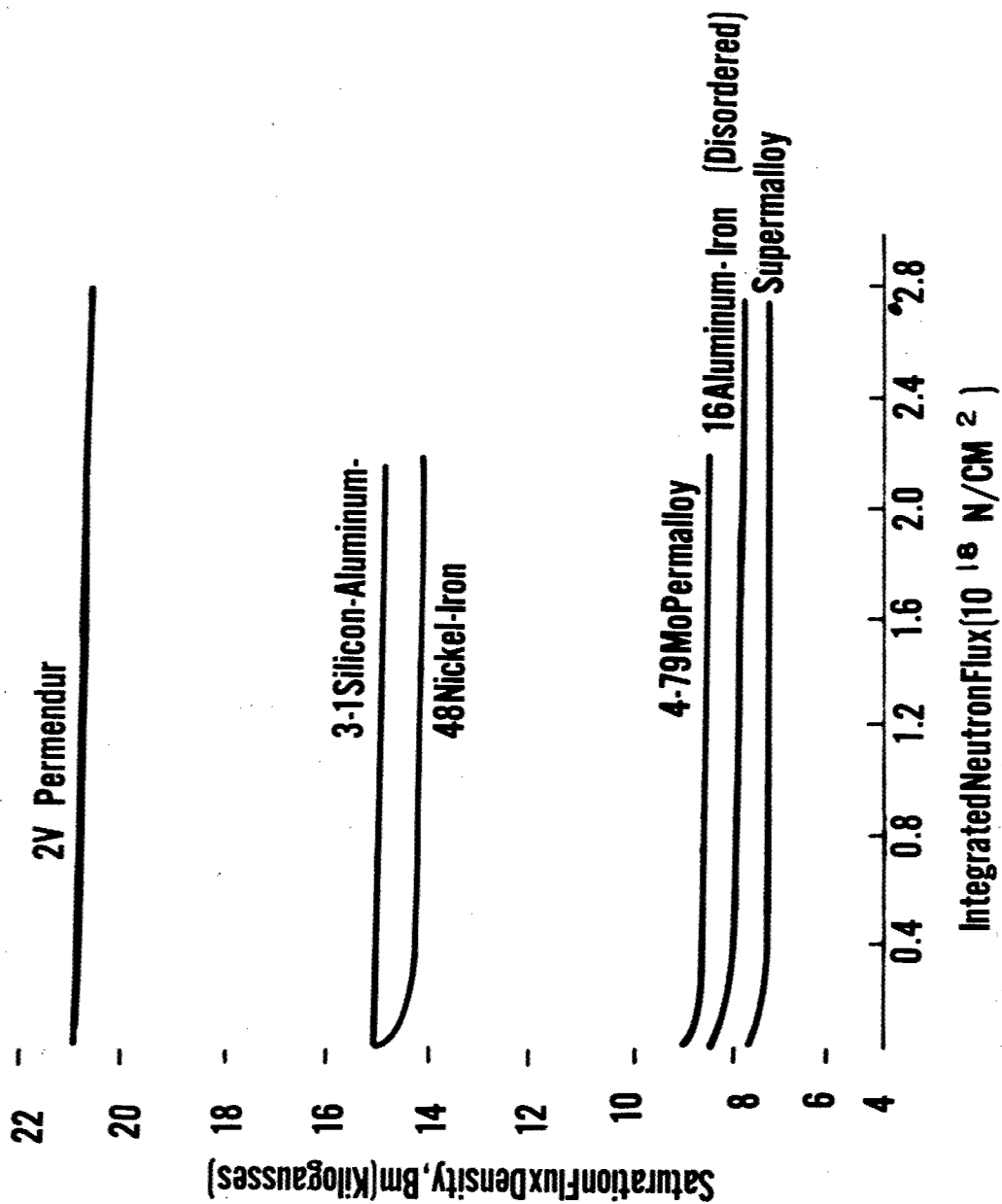


Figure 3.

EFFECT OF RADIATION ON COERCIVE FORCE

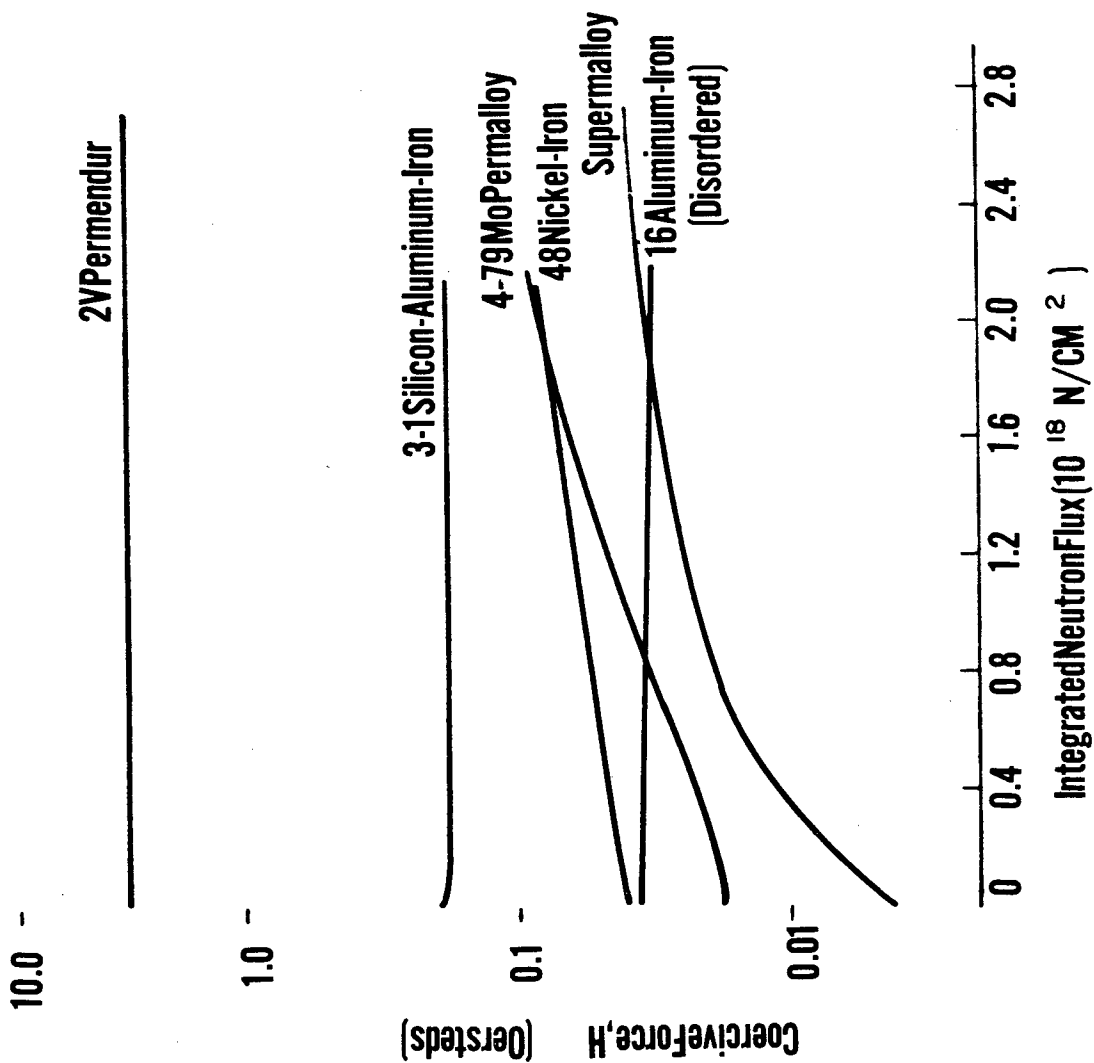


Figure 4.

EFFECT OF RADIATION ON INITIAL PERMEABILITY

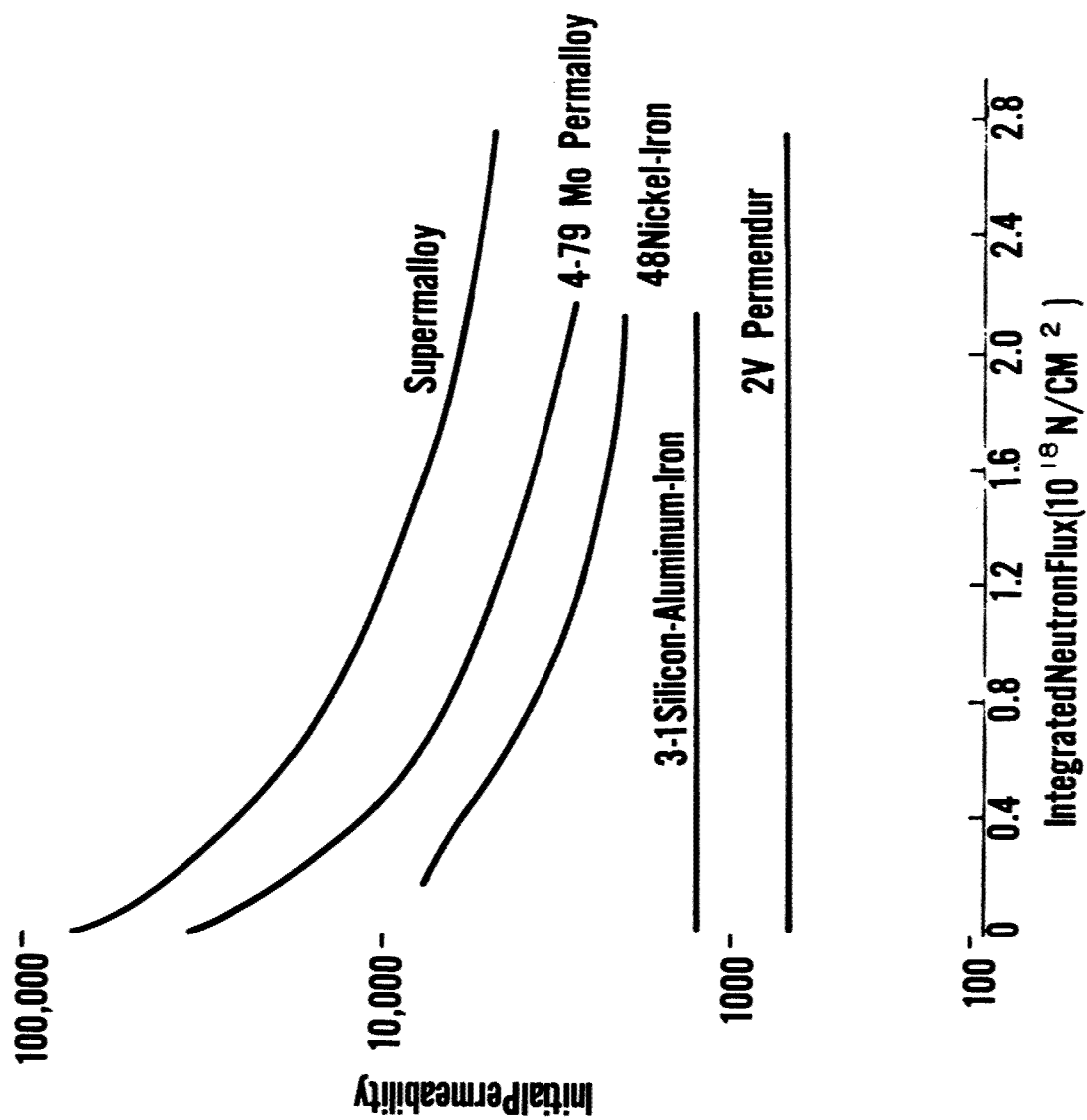


Figure 5.

EFFECT OF RADIATION ON MAXIMUM PERMEABILITY

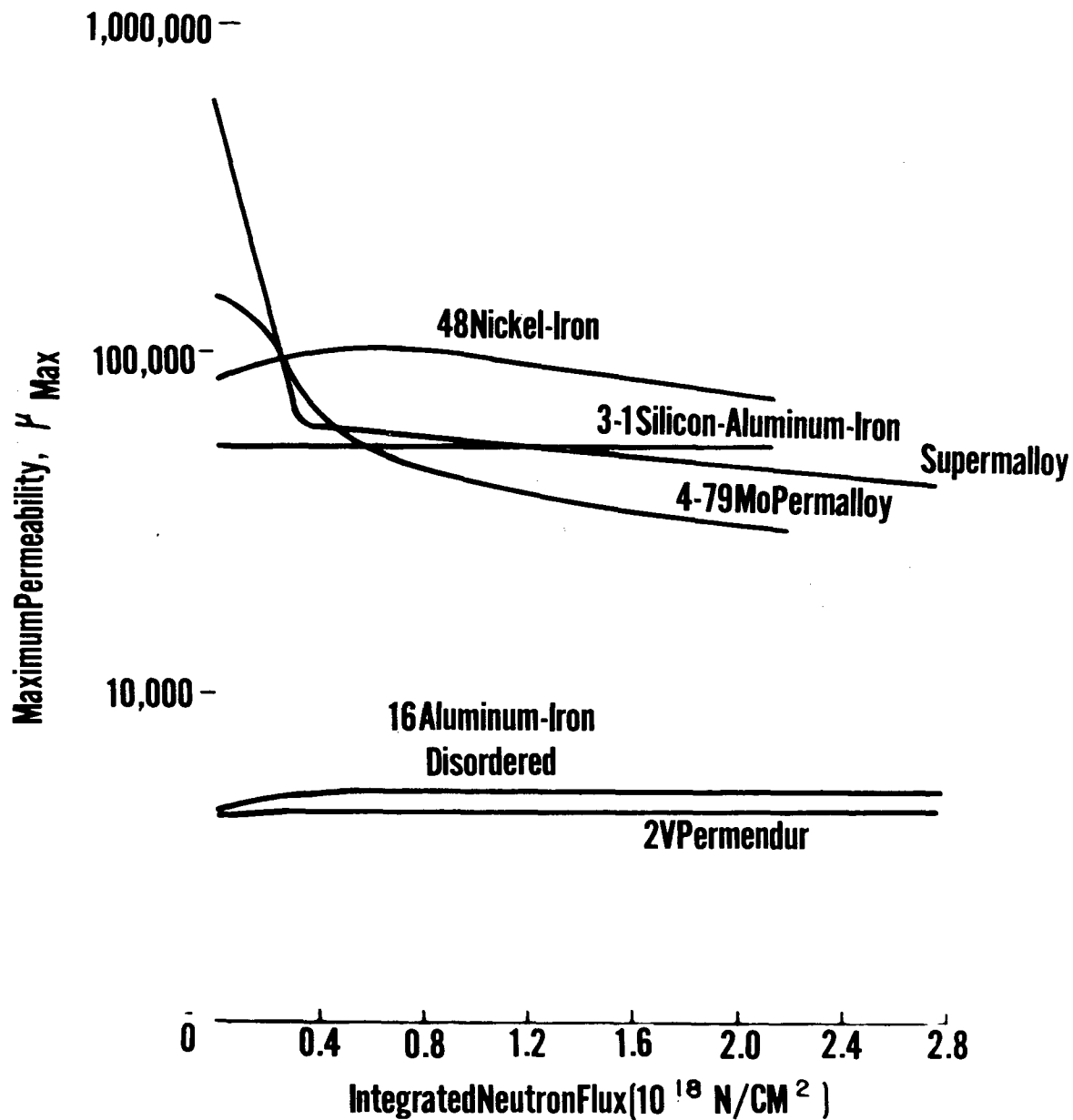


Figure 6.

EFFECT OF TEMPERATURE CYCLING ON SUPERMENDUR

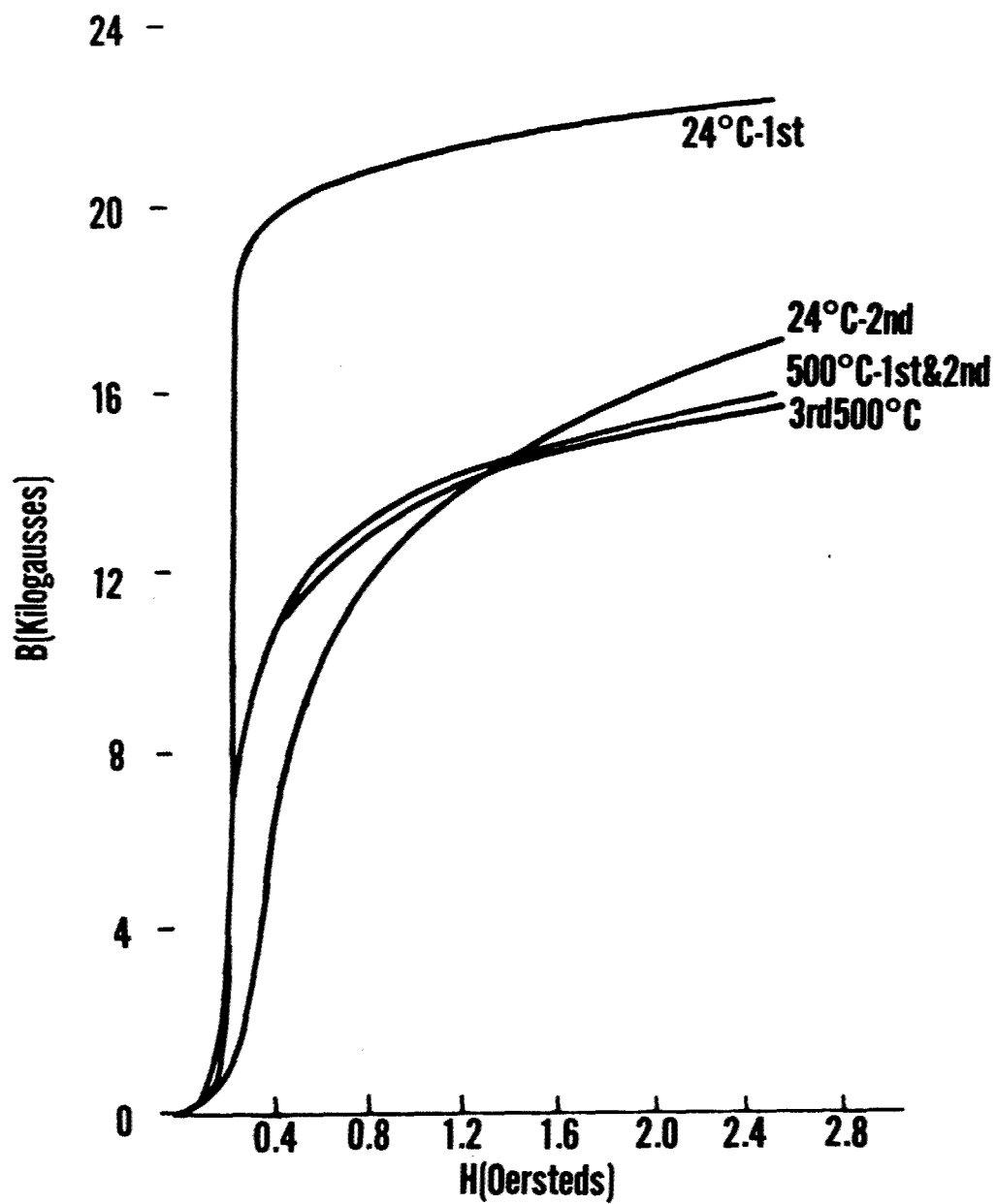


Figure 7.

EFFECT OF TEMPERATURE CYCLING ON 50 NICKEL-IRON

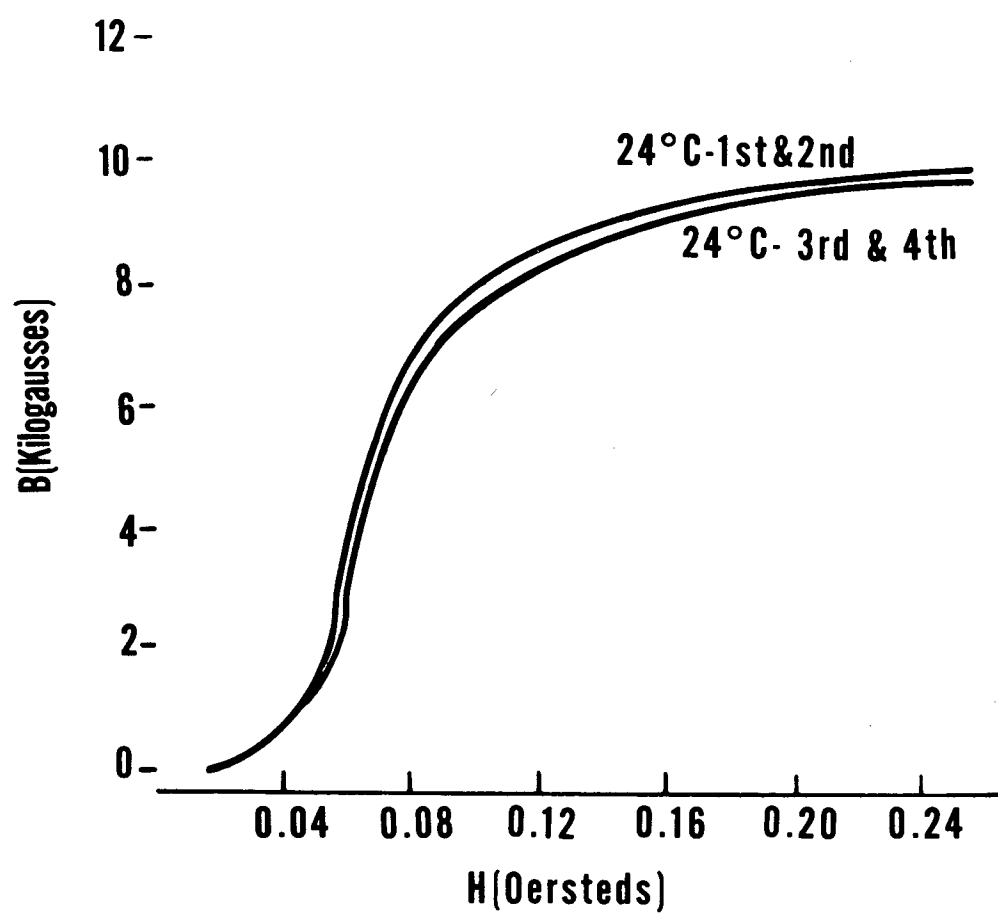


Figure 8.

ELECTRONIC MATERIAL REQUIREMENTS

F. E. Wenger

Andrews Air Force Base, AFSC

The science of electronics is literally exploding; it has risen from nothing to the fiftieth largest industry in 30 years, and from fiftieth to fifth in 20 years and it will continue to grow. This growth was made possible by the development of materials which had specific electronic properties.

Before I look into the future I would like to borrow from the past. We owe our present technical position to a few imaginative and curious scientists whose laboratories were ill equipped by today's standards. But they had a consuming desire to experiment with certain ideas, and translate the results of their work to formulas or to postulate new concepts. These early scientists were not as much concerned with material as they were with phenomena. In other words, they used available materials and many of these were those provided by nature.

This state of affairs continued until about 1906 when Dr. Lee DeForest invented the Audion Tube. This was hailed as a major contribution to the then new art of radio; note I said art, not science, for in those days it was more of a cut and try proposition than the application of scientific principles. The proponents of the tube said it could act as a generator, as a modulator to impress a coherent signal on the carrier, and as an amplifier that could amplify very weak signals to the desired intensity, a marvelous improvement over the spark gap. The Audion could even replace galena, nature's unreliable material, as a detector. But all was not well, for the tube used existing materials which were contaminated and the container was filled with gas, which created emission problems. The deficiencies existing in the materials sparked the first research for improving electronic materials, and investigations disclosed that materials used in tubes must be very pure and free from contaminants, also that gas was not a suitable material for filling a tube. The early attempts at evacuating the tube envelope were not too fruitful due primarily to unsuitable materials. By 1909 the majority of the material problems were mitigated and for the first time the Audion Tube was a manufacturable item and its performance could be predicted.

This was not the end of tube troubles; for the metallic and insulating materials used within the tube were adaptations of commercial items, and the contaminants contained therein soon destroyed the performances of the tube. Research on tube materials soon softened this problem. So by 1916 we had by today's standards a simple hard vacuum tube. For the most part electronic parts, such as the resistors, capacitors, tubes, and transistors, procurable today are very good indeed for the purpose intended, which is not for modern military systems. Some items really appear to have no wear-out features so should have infinite life - except for the intangible unpredictable failure characteristics caused during the manufacture of the part, by its material constituents or by its eventual application into circuits. Since this symposium deals with materials, one would suppose that he could omit the manufacturing and application aspects - but in fact, he really cannot forget them. In some cases these two aspects may well determine the reliability or life of the item under discussion.

In all cases an electronic material must be as suitable to withstand the mechanical stresses of handling and processing during the manufacture of an item as it must be for

the eventual electrical stresses when it is a part of an electronic system. For example, the dielectric used in a particular type capacitor must be rugged enough to permit being wound from a large bulk spool, sliced to specific widths and wound on smaller spools, and then wound into a particular capacitor along with thin layers of metal foil. It must not pick up contaminants, crack, splinter, or pull thin in spots. When completely fabricated the dielectric must have the same qualities throughout from end to end. The metal foil interspersed between the layers of the dielectric must likewise be uniform in quality and characteristics from end to end in the finished product. If the winding of these two materials has not changed their characteristics, then one could say they were suitable for processing into the finished product.

If this finished capacitor has been made for use in essentially direct current circuits but is used in a place where high frequency currents also exist, the capacitor will heat from dielectric hysteresis losses, which in turn degrades its dielectric properties, which still further increases the losses, until the item eventually fails. Thus the application must be considered in the material make-up of an electronic part, and conversely the user must take care not to use a part for an unintended purpose.

Now, getting back to the material itself, in this case the basic dielectric material must be capable of being made into tough, durable sheets having a uniform thickness and uniform constituency throughout. It must not fray or tear when cut and must be so smooth that no air is trapped when wound with metallic foil. It must withstand a wide temperature range with a minimum change in its physical and electrical characteristics. It is only when these "musts" are met that reliability has a chance of being achieved in the final product.

The advancement of the technology of radio to about 1949 was a repetition of the experiences with the tube, that is, use conventional materials, find their weaknesses, establish a fix, cut and try, and keep on cutting and trying.

During this time many theories were expounded then lay dormant. Maybe a lot of them, for lack of a tailored material to fit the special requirement. One of these theories was concerned with the mobility and control of electrons in solid state devices. The translation of this theory to hardware required a close examination of what functions electronics must perform. From this an entirely new man made device was developed, the transistor. The transistor used a material that was expressly created to perform a specific function.

The success of this work, in overcoming many of the inefficiencies and unreliability of conventional devices opened up a new technology, the science of creating materials for specific electronic functions, or a better control by man of nature's processes to meet the challenge of more versatile electronics. We must have what Frank Oliver calls leapfrogging research; we must reach for scientists capable of looking ahead to the goals of large ultimate consequences rather than just unimaginative hole plugging.

It was only after we started using extremely high purity monocrystalline materials that we could really begin to know and understand and predict the behavior of devices made therefrom. Until that time we had been using aggregate type materials made up of a mixture of many materials - mainly physical mixtures of simple to very complex chemical compounds - both organic and inorganic. "Cook Book" technology, cut and try techniques, and the like were employed - not only in concocting the initial material itself but a similar philosophy was employed in its processing into electronic items in the eventual circuitry. The philosophies of "let's try it" and "see if it works" are still used when we should be tailoring our efforts about well known chemical and physical facts. It's high

time we learned to get away from cliches as "the operation was a huge success - but the patient expired."

The method of testing thousands of items for thousands of hours is far too costly, takes too much time and trusts too much to luck - that is, luck in that the materials and processes are stabilized and not subject to change. Such reliability testing, used on all items that must be extremely reliable, is too great a burden for the country's economy to bear. The real solution is to make our materials so stable, so homogeneous, so consistent, that reliability is a natural with standard automated processing and sound application.

I have attempted to illustrate the idea that further advances in electronics will be limited by the advances made in electronic materials, and this points up various areas which must be investigated if we want our material technology to lead our operational requirements. I would like to discuss a few of these at this time. My remarks will be limited to the broad and long range concepts, specific hardware will be covered by speakers who will follow me.

Reliability of Electronic Materials

One of the greatest problems that confronts us today is the reliability of our electronic equipment. It will not be possible to perform the contemplated military or space functions of the future with electronic equipment having mean time to failure of 3-5-10-50-100 or 1,000 hours. We must think of mean time to failure in the order of 10,000 - 50,000 and 100,000 hours. This will require that certain materials used in parts or subsystems must have failure rates of less than .0001 percent per 1,000 hours operations. Note I stated materials not parts, for behind each part failure lies a material failure, also future electronic systems will in all probability be designed with functional blocks, wherein the electronic parts as we know them today will lose their separate identity and the part phenomena will be grown as part of a solid block. Research is needed to acquire an understanding of the molecular behavior of materials under static or dynamic conditions, and how this behavior contributes to failure. I would like to quote from the 1961 Book published by DOD titled "Important Areas of Electronic Research."

"Reliability of components must be based on a deep understanding of the materials and processes that go into their fabrication. Much good work is being done to achieve this understanding, and on its success the reliability of future large weapon systems depends. I therefore rate the basic work toward achieving this understanding as the most important contribution toward reliability."

I have been subscribing to this premise for the past 15 years and it is good to see others striving for the same purpose -- that is, a better understanding of the properties of matter, how to control and how to use them. Just pause for a moment and visualize the tremendous electronic materials research effort implied by the simple title -- Reliability of Electronic Materials.

Solid State Research

Certain aspects of germanium and silicon materials for transistors appear to have sufficient emphasis placed on them, but we seem to be a nation of research followers rather than a nation of independent research thinkers. As result of this we find many capable researchers waiting for somebody else to spark the idea and he then will get on the bandwagon and never seems to know when to let loose and pursue something new. We need a greater percentage of our scientists to be bold new creators rather than docile

followers. Let's take some of the research energy we are directing toward silicon and germanium and direct it toward looking for new phenomena, rather than incrementally improving material or duplicating some other scientists' effort. Let us broaden our solid state research to include stability, low temperature operation, and fabrications to pre-selected specifications.

It would appear that one of the payoff efforts would be to forget about electronic construction as we know it today, and break down electronic functions into various phenomena such as generation, amplification, mixing, modulation, demodulations, display, and synthesize black-box electronic function from physical processes.

Laser

We found the material for the operation of the laser by chance, not design, I cannot help wondering how much further ahead we would be if our materials people would have anticipated this need and had the material knowledge waiting for the application. As it is, now that the principle has been established, we must concentrate research on suitable materials. What can we do with such a material? The ability of the laser to transfer efficiently the broad band energy into the energy of a single optical line, makes it possible to concentrate the emergent coherent light to a fine focus and to achieve effective communication, point to point transmission of power, or concentrate a tremendous amount of energy at some distant point. This is food for thought.

Radomes

The problem of material for electrically transparent housings has never been adequately solved.

Super Conduction

Basic work is needed on alloys that act as super conductors at normal temperatures without the basic materials being super conductive.

Super conductors which exhibit magnetic properties are desired.

Ceramics

Flexible ceramics with high insulating resistance in the microwave area would be a worthwhile project. Specialized materials for specific application which do not require doping are desired.

Organic Semiconductors

These open up a whole new research area.

Materials for Electron Tubes

The day of the simple glass enclosed electron tube is nearing an end. During its heyday, very clever automated machinery with fairly reasonable controls, made the glass envelopes, hermetically sealed in the various internal structures that could withstand a fairly wide temperature range, tested and packaged the final product. Semiconductor items are replacing these receiving tubes for three very potent reasons: size, overall cost and reli-

ability. The new tubes of Air Force interest are not simple amplifying or oscillating devices. Rather they have become complete electronic subsystems needing in many cases only a power supply and an antenna. They are going to get even more complex as time goes on. Higher power and higher frequencies, bandwidth, and tunability are some of the more simple goals. Structures are metal and ceramics, both of which must be non-porous, withstand extreme temperature ranges and be rugged enough to withstand the mechanical stresses encountered in aerospace systems.

Ceramics are used to provide electrical insulation. However, good electrical insulators are also good heat insulators. High power requires that tubes handle and dissipate a great deal of heat. Therefore, the ceramics used in tubes should be a good insulator for electricity and a good conductor of heat. Ceramics generally are not such good electrical insulators at high temperatures, hence this places another requirement on the ceramic. Still another, it must not absorb microwave energy, and that is the type of tube we are mostly interested in for millimeter and submillimeter waves.

Since tubes are made of ceramic and metal and are still vacuum inside, there must be a vacuum tight seal or bonding between the metal parts and the metal to ceramic parts. Here again cut and try techniques are used. The chemistry and physics of the surface and sub-surface properties of such bonding should be thoroughly studied to determine the reactions involved and the optimum procedure to be employed to achieve vacuum seals, keeping in mind that during processing the parts may reach temperatures of over 1000°C and after completion may cycle from -65° to +750°C.

Many of these tubes require external magnetic elements to control the path of electrons flowing within the tube. Here the needs may be stated as:

- a. Coercive Force - The need is for a constant or nearly constant coercive force versus temperature curve. Temperature range -65° to a minimum of 250°C. Also higher coercive forces are needed.
- b. Nuclear Radiation - Most of the high coercive strength material contains cobalt. Cobalt has a long half life. Need is for material which does not retain radioactive properties after radiation exposure.
- c. Periodic Focusing - The Alnico series so far have not been usable to periodic focusing of traveling wave tubes. Ferrites have been used extensively. The need is for a light weight material with Alnico's flat coercive force versus temperature characteristic and the ferrites' machinability and ability to retain magnetic field under shock and vibration.

Other Tube Problems

There are other tube problems with the possibility of solution by studies as indicated below:

- a. Study of high strength metal whiskers for storage screen mesh in image tubes.
- b. Study of high strength dielectric material whiskers for storage mesh in memory tubes.
- c. Study of Electrets for memory tubes.

- d. Study of single crystal selenium and other possible materials of high resistive property for EBIC Camera Tube.
- e. Study of secondary emitting properties of materials used in Imaging and Memory Tubes.
- f. Study of photo emission.
- g. Study of electron bombardment induced conductivity in dielectric materials for imaging and memory tubes.
- h. Study of material photo emissive in visual octave and photo conductive to the infra-red octave of the electromagnetic spectrum.
- i. Search for anisotropic resistive material for use in image storage tube target.
- j. Search for anisotropic material as a substitute for fiber optics and as a substrate for photo sensitive - phosphor sandwich used in image amplifier tubes.

Solid State Materials

I have covered only a few items. There are many thousand more, an infinite variety of thin films in all possible variations and forms either as single or multilayer films to give electronic functions and eliminate inter-connections, which is one of the biggest problems we have in electronics. In studying the mechanical properties of materials we may discover the secret of long life. The field of materials research is as broad as your initiative. It is one field in which you cannot do research by ballyhoo. Your results must be accurate and informative and free of all gimmicking. I could point to some recent publicity releases and papers which made unwarranted claims, and questionable use of terms and distortions of scientific concepts, and state this type of ballyhoo does not add anything to the scientific literature, but does a lot of harm, by instilling a false sense of well being in top management, and colors their decisions on critical problems. I think a fitting close for this presentation would be a condensation of Mary Alice Hilton's remarks on keeping an open mind, "Most of us have become immune to miracles, we are inundated by them. There are miracle electronic devices, miracle drugs, miracle computing machines, all the other 100 miracles. To this array we would like to add just one more (Very Special) miracle, it is positively the last, for it is the miracle of all miracles. It is the miracle of the not yet discovered and the not yet invented. The miracle of the not yet known, and the not yet tried, the miracle of the not yet experienced and the not yet achieved, the miracle of all the machines we have yet to build, all these appear to have one catalyst, that makes it happen, an open mind, to find irresistibly fascinating peaks where others have trudged along a plane of monotony."

DIELECTRIC MATERIAL

Chairman

Mr. Wittebort

Speakers

Mr. W.G.D. Frederick

Dr. G.F.L. Ehlers

Capt. Metscher

Panel Member

Mr. R. Larson

DIELECTRIC MATERIALS FOR ADVANCED ASTRONAUTIC WEAPONS SYSTEMS

W.G.D. Frederick

J.I. Wittebort

Directorate of Materials and Processes, ASD

Introduction

We have a better insight today into the technical problems and materials requirements confronting us for advanced aeronautical and space vehicles over what was voiced in 1958 at the Materials Symposium in Dallas. Since that date many long range ballistic missile flights, orbital and space probes, and orbital payload recoveries have been accomplished with varying degrees of success. These pioneering activities have done much to sharpen our understanding of the various materials problems, an understanding of which has helped us to delineate more sophisticated approaches toward accomplishing greater feats.

The purpose of this paper is to outline the environmental conditions under which high temperature dielectric materials might be expected to operate, the potential uses and materials requirements in various engineering devices of Air Force interest, the state of the art in this materials area, and the possible advances that could result from basic and applied research activity.

Further advances in high temperature dielectrics are required in the following important areas:

Re-entry Radomes

Thermionic Energy Converters

Ion Propulsion Engines

Radio and Microwave Frequency Generators

Capacitors for Energy Storage

Insulation for High Temperature Conductors

Corona Suppression

Radar Camouflage

Hopefully, materials requirements for these diverse uses can be met simultaneously by a concerted basic and applied research assault on a few well chosen materials followed by a technological program to produce them in the desired shapes and quantity. In general, the materials available for high temperature mechanical applications are not of sufficient purity, form, or reliability to meet the existing requirements. The basic studies on the nature of brittle fracture, and increasing the thermal shock resistance of ceramic systems should be followed closely.

The High Temperature Environment

The many analytical and experimental studies made for various possible astronautic systems tell us that the re-entry phase is the most demanding upon materials from the heat transfer standpoint while the launch and space phase are most demanding from the reliability and operational performance standpoints.

Figure 1 outlines the heat transfer environment expected for ballistic and manned vehicles re-entering the earth's atmosphere under various trajectories. The ballistic trajectories result in very high heat transfer rates ranging from 1000-5000 BTU/ft² - sec, depending upon the magnitude of their ballistic parameter or fineness ration. These heat transfer rates result for only 30 seconds or so and occur at relatively low altitudes. Heat sink and ablation techniques have been used primarily to thermally protect these vehicles from destruction during the re-entry phase. This poses a very serious problem on telemetering antenna and communication devices for this type of weapons system. Manned vehicles, because of "g" limitations, must necessarily re-enter the earth's atmosphere more gradually resulting in re-entry times of about 30 minutes, and in heat transfer rates of 10-100 BTU/ft² - sec, considerably reduced, but still very serious when you consider the high temperatures and times involved. Radiation and transpiration cooling appear to be the most desirable methods of thermal protection for these vehicles. Here again antenna housings, radomes, and other dielectric materials next to the boundary layer are exposed to conditions during operation never before investigated.

Figure 2 shows an estimate of the temperature conditions to be experienced by various parts of a manned boost glide re-entry vehicle using the "hot structure" concept. Under the most favorable circumstances present high temperature dielectric materials will be on the fringe of usefulness unless they are located in refrigerated area. It is for this primary reason that we are investigating and improving the temperature limits of high temperature dielectric materials.

Current Technology on Dielectric Materials

Radomes: In supersonic guided missile and space vehicle applications the radome must withstand not only high temperatures, but also severe thermal shock, sudden aerodynamic pressures, vibrational and destructive erosion forces which form its in-flight environment and reach adverse peaks during re-entry. The satisfactory solution of these problems is fundamental to the success of the manned re-entry concept. Table 1 and figures 3 and 4 outline the known properties of several dielectric materials for high temperature antenna housings and radomes. High purity fused silica, alumina, and beryllia appear to have many of the necessary high temperature, thermal shock resistance, and electrical properties necessary for some of the antenna and radome housing applications. The electrical properties of these materials are incomplete and the reliability unknown because it is extremely difficult to make these measurements, especially at microwave frequencies and at elevated temperatures.

A program has been initiated to extend dielectric measuring techniques and apparatus up to temperatures of 3000°F and frequencies up to 50 kmcps to characterize existing dielectric materials. This program will provide long range research into the development of new dielectric materials for use at temperatures of 3000°F and above by attempting to find atoms, molecular groups, and crystal structures which offer materials of special promise for high temperature applications.

Several previous ASD programs which were directed toward the production of high purity dielectric materials should be useful in planning future development work in these areas. In one of these programs, high purity alumina ceramics (having less than 100 ppm impurities) were prepared and some of these were deliberately contaminated by foreign ions. The objective behind the preparation of this series of pure and contaminated ceramic specimens was the isolation of the effects produced by each impurity ion on the dielectric properties of alumina. This information was statistically deduced from measurements of loss tangent and dielectric constant in the frequency range from 10^2 to 10^7 cycles per second and temperatures from 80 to 930°F. A multiple regression analysis of the electrical data provided by these doped specimens has shown that in the order of diminishing influence, the impurities may be grouped as follows: Si, Mg, Ti, Ca, Cr, and Fe (see figure 5). It was also found that high purity alumina has nearly the same positive temperature variation of dielectric constant as far less pure commercial alumina ceramics. Since purification alone was not effective, achieving an invariant dielectric constant was approached by the expedient of introducing into the alumina a second phase having a negative temperature variation of dielectric constant. Since titanites are the most common compounds having the desired negative temperature coefficient; it only remained to choose a representative which would not react with alumina at high temperatures. Fortunately, because the titanite group is more electronegative than the aluminate, such compounds as CaTiO_3 and SrTiO_3 remain as a stable second phase when fired with the alumina. Preliminary results have shown that a composition containing 10 percent CaTiO_3 and 90 percent alumina has an invariant dielectric constant up to about 480°F at 10^7 cps, and losses at 930°F and 10^7 cps somewhat lower than those of Pyrocera 9606.

Another program has been directed toward the preparation of high purity inorganic dielectrics which should possess optimum electrical properties at 1000°F to make them suitable for capacitors and insulators. To obtain optimum properties, inorganic materials for high temperature use must be free of impurities and voids. Elimination of impurities from starting materials as well as the prevention of their introduction during fabrication of the materials into useful forms have been emphasized. Following these principles, good high temperature dielectric properties have been produced in molded or sintered blocks of alumina and boron nitride.

This work on improved high temperature dielectrics for radomes has direct bearing and application to the dielectric materials requirements for thermionic and magneto-hydrodynamic energy converters, for ion propulsion devices, and high powered radio and microwave tubes.

Capacitor Materials

The same problems of maintaining purity were encountered, even to a greater degree, in preparing thin films of these materials in a usable and measurable form for capacitors. Thin dielectric films are particularly subject to the effect of imperfections on their properties since the size of such defects, whether they are projections of the metal electrodes or impurity particles, may be of the same order of size as the thickness of the film. For this reason the dielectric properties measured on these films may be grossly affected by these imperfections, in addition to any more generally distributed impurities.

Another characteristic of thin film dielectrics is the greater prominence of interfacial ionic polarization effects, particularly in anodized aluminum. It has not been possible to duplicate the electrical properties of the high purity sintered block material in thin films, however, relatively good dielectric properties have been achieved in these thin films. Another phase of this program was to study thin films prepared by the relatively new technique of arc plasma jet spraying. In this method, a stream of argon gas is passed through an arc where it is ionized and heated. Alumina powder is vibrated into the jet stream where it is heated almost to its melting point and then transported at high velocity to the metal surface where it is embedded. However, a contamination problem from the arc electrodes and nozzle was encountered and the electrical properties of the oxide films were poorer than those of sintered discs made from the same powder.

Corona-Resistant Materials

In addition to the temperature requirement imposed by high speed flight, the behavior of electrical materials exposed to the highly ionizing conditions met in the operation of flight vehicles at very high altitudes must be considered. Commercially available electrical materials tend to outgas under low pressures (200,000 feet altitude or 2mm of Hg absolute), especially under conditions of elevated temperature. As the dissolved gases and volatile components escape, the insulation deteriorates and electrical breakdown and arcing may result. Therefore, electrical equipment which is well designed for ground operation may not operate at all at higher altitudes.

The degree to which electrical insulating materials are attacked by corona seems to depend upon the intensity of the corona discharges, the pulse shape and duration, the time under corona, the surface conduction and charge distribution on the insulation, the environmental gas, its temperature, pressure and flow, and the chemical nature of the insulating material itself. An applied research program is underway to obtain some measurements which reflect the extent of damage which takes place under various corona conditions on a number of insulating materials and to obtain information which will reveal the type of chemical reactions which take place. These results will be analyzed to obtain information about the mechanism of chemical reactions resulting from corona degradation and their relationship to the electrical nature of the discharge and the physical and chemical properties of the insulating materials and their environments.

Insulation for High Temperature Conductors

The ever increasing speeds developed and anticipated by air and space vehicles are creating higher and higher ambient temperatures. Electrical components operating under these higher temperature conditions are seriously handicapped by the lack of suitable insulating materials.

One approach to the problem of high temperature wire insulation is to combine an organic and inorganic coating in the form of a resin containing a powdered glass filler, the resin providing the necessary flexibility. When the insulation system is heated to a high temperature, the resin should burn out and the powdered glass should fuse forming a continuous coating to 1500°F. At 500°F, however, a vitreous enamel coating had poor electrical properties unless a stand-off insulator was provided to keep the viscous molten coating from contact with the bare wire. Aluminum oxide in the form of an anodized coating was selected as the most promising stand-off insulation. This wire was capable of operation at 800°F.

Insulation research at Bell Labs has uncovered a way of forming fluoride coatings on copper, aluminum, and other wire metals that provide excellent insulation at temperatures approaching the melting point of the conductor itself. Even at these temperatures, the insulation is said to retain flexibility and freedom from porosity.

These insulating coatings are formed directly on freshly-cleaned copper or aluminum exposed to the oxidizing carriers of hydrogen fluoride or elemental fluorine at 570 - 1190°F. The thickness of the resulting film depends on the forming temperature, concentration of fluorine, and the exposure time. Aluminum forms a fluoride film that becomes one micron thick in a few moments at 1020°F. The film is reported to adhere to the wire even when bent repeatedly at a 90-degree angle.

According to Bell Labs, the electric insulation values for copper and aluminum films 1-2 microns thick are on the order of 10^{10} and 10^{11} ohms at room temperature. The aluminum fluoride insulation resists breakdown at 450V at 930°F. (The best organic insulation coatings cannot be used continuously above 570°F.)

A porcelain type ceramic coating applied directly to the bare copper wire is another approach. CuO has been incorporated in the base coating and this incorporation has improved the electrical properties. Sheathing these vitreous coatings with organics showed promise as a method for retaining the flexed vitreous coating on the wire.

Radar Camouflage

The Air Force is conducting an active program in radar camouflage, which is concerned partly with the development of radar absorber materials (RAM). Some of the problem areas facing the radar absorber materials designer appear to be solvable only through fundamental materials research.

Generally, radar absorbers depend upon the magnetic and/or dielectric properties of constituent materials to provide electromagnetic impedance matching at the outer surface and dissipation of energy internally. Matching at the outer surface is necessary to insure penetration, and not reflection, of incident energy; since only that energy which penetrates the material may be dissipated.

The required combination of matching and dissipation implies the magnetic and dielectric properties to be complex quantities. These are usually characterized as:

$$\text{permeability } (\mu) = \mu' - j\mu'' \text{ (magnetic properties)}$$

$$\text{permittivity } (\epsilon) = \epsilon' - j\epsilon'' \text{ (dielectric properties)}$$

where μ' and ϵ' are the real parts and μ'' and ϵ'' the loss factors. The degree of freedom in absorber design is directly dependent upon the ability to exercise independent control of these four parameters.

Absorbers containing magnetic materials ($\mu > 1$ relative to air) have thus far received only moderate attention from engineers intent upon applying RAM to aircraft or missiles because of weight penalties. On the other hand, thicknesses are orders of magnitude below those of absorbers containing no magnetic materials. For this reason, considerable effort should be devoted to development of magnetic absorbers with the hope that weights can be ultimately reduced to useful values. The desirable magnetic properties are usually

derived through the use of ferrites (here defined as materials which fall in the broad category of magnetic oxides.)

The state of the art today permits design of high quality RAM with a variety of available ferrites as possible constituents. The big problem, however, is achieving effectiveness over broad ranges of radar frequencies. Limitations on bandwidth are a direct result of the variation of ferrite properties with frequency. The basic factors which determine the ferrite frequency response are not understood precisely, hence there is little knowledge of (a) what determines the μ' and μ'' of a ferrite and (b) what one can do to construct new ferrites with predetermined characteristics. Additionally, RAM containing ferrites are plagued with problems associated with the environment in which it must be used i.e. temperatures which exceed the Curie point, vibrations and strains which reduce the often brittle materials to powder. Only basic research can solve these problems. These ferrite radar absorbing materials could be expected to be useful in the suppression of near field radio and microwave interference also, especially in those installations where several electronic systems are operating in close proximity.

We turn now to radar absorbers which contain no magnetic materials and which are designed on the basis of controlled dielectric properties. That such absorbers exist commercially today is evidence of the variation in constituent materials which is tolerable in the design.

These "controlled dielectric" radar absorbers are inherently thicker than the previously mentioned magnetic types but have several major advantages; they are much lighter weight; have broader bandwidths; and have a flexibility in design which permits choice of constituent materials so that the composite RAM has the desired mechanical and environmental properties.

To design such materials, one needs constituents having a dielectric constant from 1 to 20 and a loss factor from 0 to 20. The maximum values are not exact, but only indicate the range required. To achieve these permittivities today, the normal technique is to impregnate low dielectric constant materials, which act as support matrices, with others of high dielectric constant and high loss. By controlling the concentration of the impregnant, control of the dielectric constant and the loss factor of the finished product is attempted. The addition of certain types of carbon have been found to yield the desired range of values of dielectric properties when combined with a given matrix material. A major reason for an inability to improve the RAM is the inability to control the distribution and concentration of the carbon to the point where predictable and repeatable results can be obtained. Metal particles in place of carbon do not appear to be useful because increasing concentration causes no significant increase in conductivity (which is a measure of the loss factor) until a point is reached where a small increase in concentration causes an extremely rapid rise in conductivity. This occurs when the concentration is great enough to produce electrical contact between particles.

Apparently, a material is needed which is a true semiconductor and which is well-ordered. Carbon is a semiconductor but the best type for RAM use is random in shape and size and therefore it is difficult to control its electrical properties. Research to develop a new semiconducting polymer would appear to be a solution to this problem at least for intermediate temperature applications.

Conclusions

Military requirements are steadily emphasizing operation at higher altitudes and under all weather conditions, as well as requiring these operations to be performed almost completely by automatic equipment. This places stringent requirements on the stability and reliability both in the physical and dielectric properties of materials over a temperature range of -85 to 500°F on current airborne electronic equipment and on re-entry vehicles. This upper temperature limit may extend to 3000°F .

The dielectric materials required for 2500°F antenna housings of Dyna-Soar type re-entry vehicles appear feasible and obtainable with present technology. However, further work in the development of new dielectric materials able to withstand temperatures above 3000°F , as well as characterization and evaluation of these new materials under simulated operational conditions will be necessary to meet the operational requirements for future weapons systems. These high temperature dielectric materials will also be useful as insulators for thermionic and magneto-hydrodynamic converters, for ion propulsion engines, and for high powered radio frequency and microwave generators and amplifiers.

With the growing interest in the sub-millimeter wavelength and infrared region, it is also necessary to consider window materials which will be suitably transparent to these wavelengths yet compatible with the environmental operating conditions of these advanced weapon systems.

With regard to future work on high temperature capacitors, it appears to be necessary to develop new ferroelectric materials and solid solutions which will have higher Curie temperatures than presently available ferroelectric materials, as well as producing high quality thin films of these materials for microminiaturized components.

Further work on high temperature wire insulation is required to develop techniques for applying adherent inorganic dielectric coatings to high temperature conductors and still retain flexibility up to 2000°F .

The development of radar absorber materials is dependent on the complete control of the electromagnetic properties of materials. The theory of design for many types of absorbers is well documented; but until stable materials can be developed and fabricated reproducibly into components having the desired properties, little can be done to improve the current status of radar absorber materials.

BIBLIOGRAPHY

1. Armour Research Foundation, "Research and Development Services Leading to the Control of Electrical Properties of Materials for High Temperature Radomes," WADC TR 59-300, Parts I, II and III.
2. Westinghouse Research Labs, "Synthesis and Purification of Dielectric Materials," WADC TR 59-337, Parts I, II and III.
3. Battelle Memorial Institute, "Investigation of Sinterable Powders and Properties of Beryllium Ceramics," WADD TR 60-108, Parts I and II.
4. University of Illinois, "High Temperature Electrical Insulating Inorganic Coatings on Wire," WADC TR 58-12, Parts I, II and III.
5. Georgia Tech, "High Temperature Insulation for Wire," WADC TR 58-13, Parts I, II and III.
6. Emerson and Cuming, "Silica Microbubbles," WADD TR 60-899, Parts I and II.
7. IRE Newsletter for the Professional Group on Component Parts, August 1960.

TABLE I HIGH TEMPERATURE DIELECTRIC MATERIALS							
MATERIAL	MELTING POINT (°F)	SPECIFIC GRAVITY	THERMAL EXPANSION (%)	TOTAL EMISSIVITY	THERMAL CONDUCTIVITY BTU/HR/FT/°R	DIELECTRIC CONSTANT (8.4 KMC)	LOSS TANGENT (8.4 KMC)
FUSED SILICA (SiO ₂)	3100	1.9	RT 0.10 2000°F 1.35 2500°F 1.40	0.87 0.40	0.9 1.3	3.17 3.28 3.42	0.0002 0.007 0.012
ALUMINUM OXIDE (Al ₂ O ₃)	3700	4.0	RT 0.05 1500°F 0.60 2000°F 0.95 2500°F 1.10	0.78 0.58 0.50 0.44	19.0 4.0 3.2 3.0	8.8 10.1 10.6 11.1	0.0001 0.0004 0.0027 0.0135
BERYLLIUM OXIDE (BeO)	4650	3.0	RT 0.00 1000°F 0.40 2500°F 1.20	0.56	138.0 34.0 10.0	6.24 6.56	0.0004 0.0005
GLASS CERAMIC (PYROCERAM 9606)	2460	2.6	RT 0.00 1000°F 0.25 1500°F 0.36	0.85 0.72 0.67	0.15 1.20 1.30	5.4 5.4 5.4	0.0003 0.002 0.02

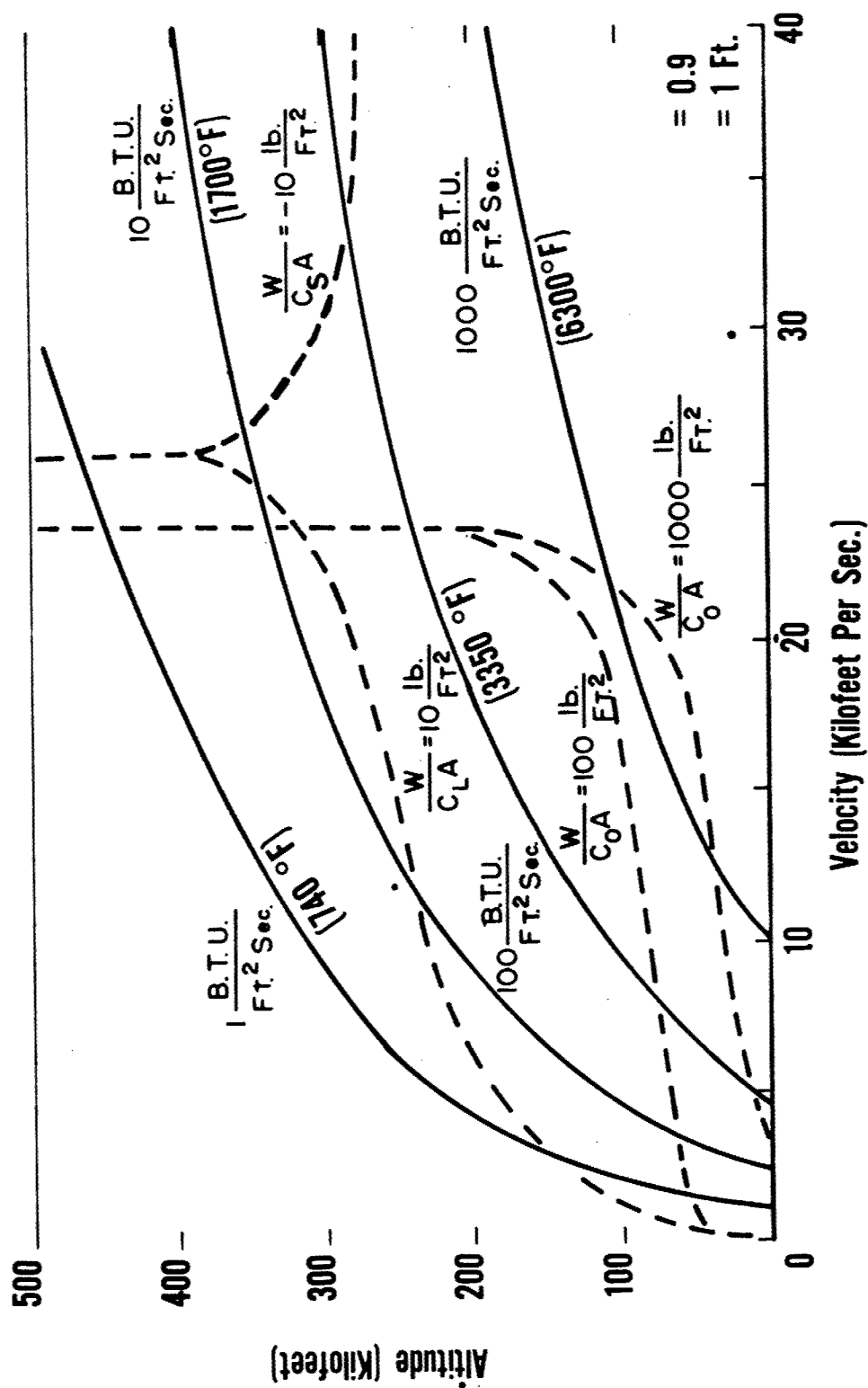


Figure 1.

TEMPERATURE LIMITS FOR HYPERSONIC RE-ENTRY VEHICLES

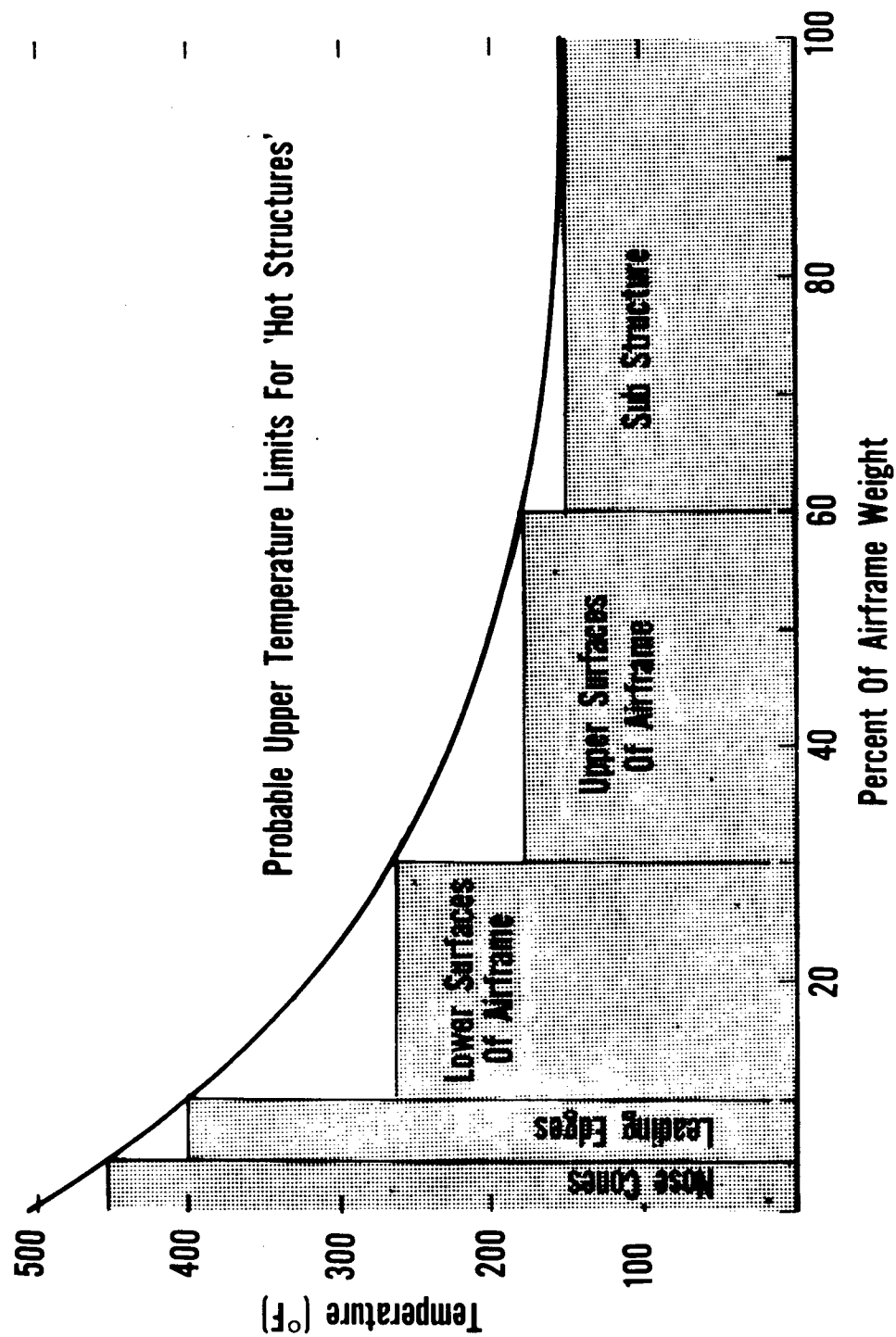


Figure 2.

LOSS TANGENT vs. TEMPERATURE

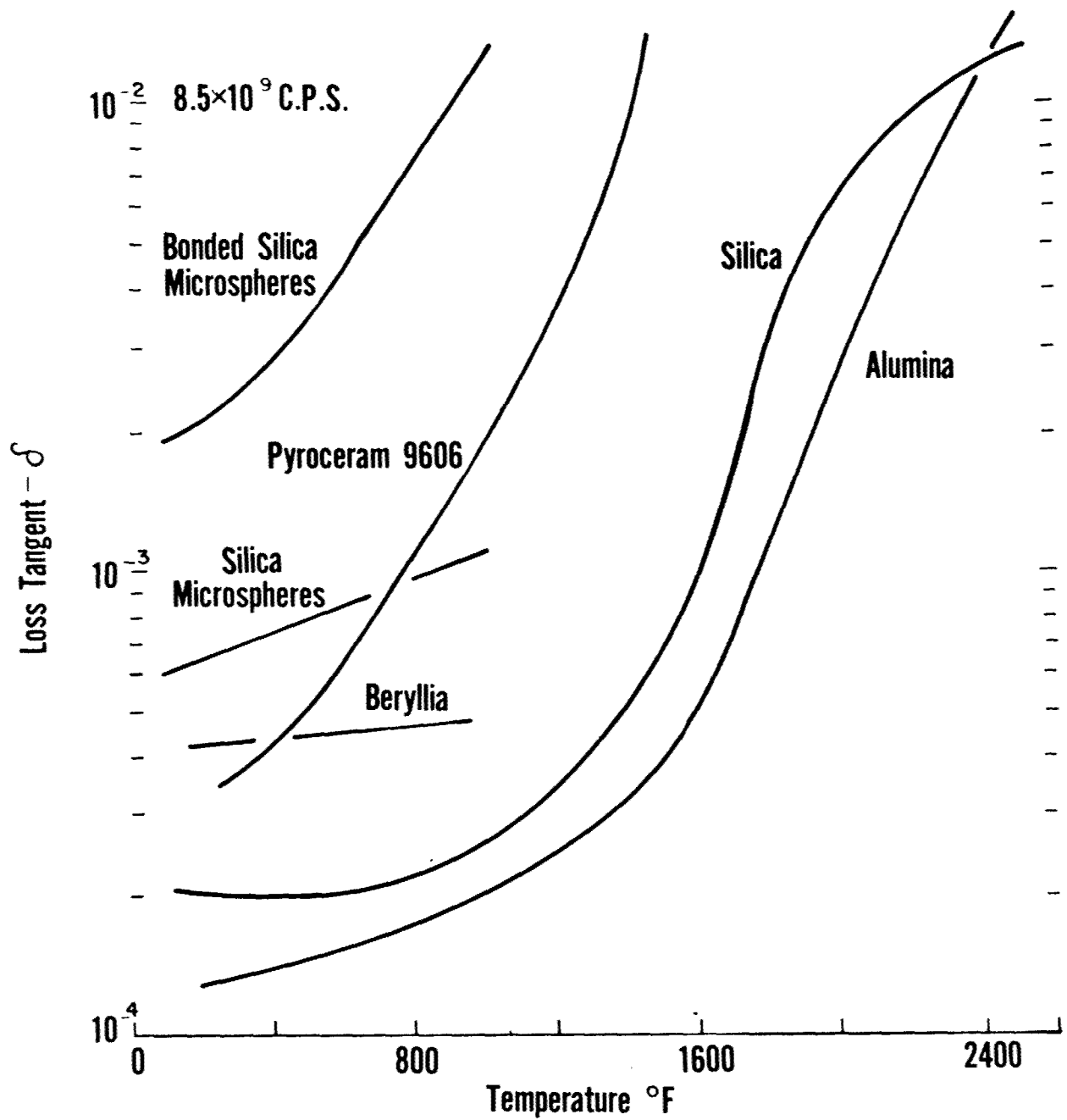


Figure 3.

DIELECTRIC CONSTANT vs. TEMPERATURE

8.5×10^9 cps

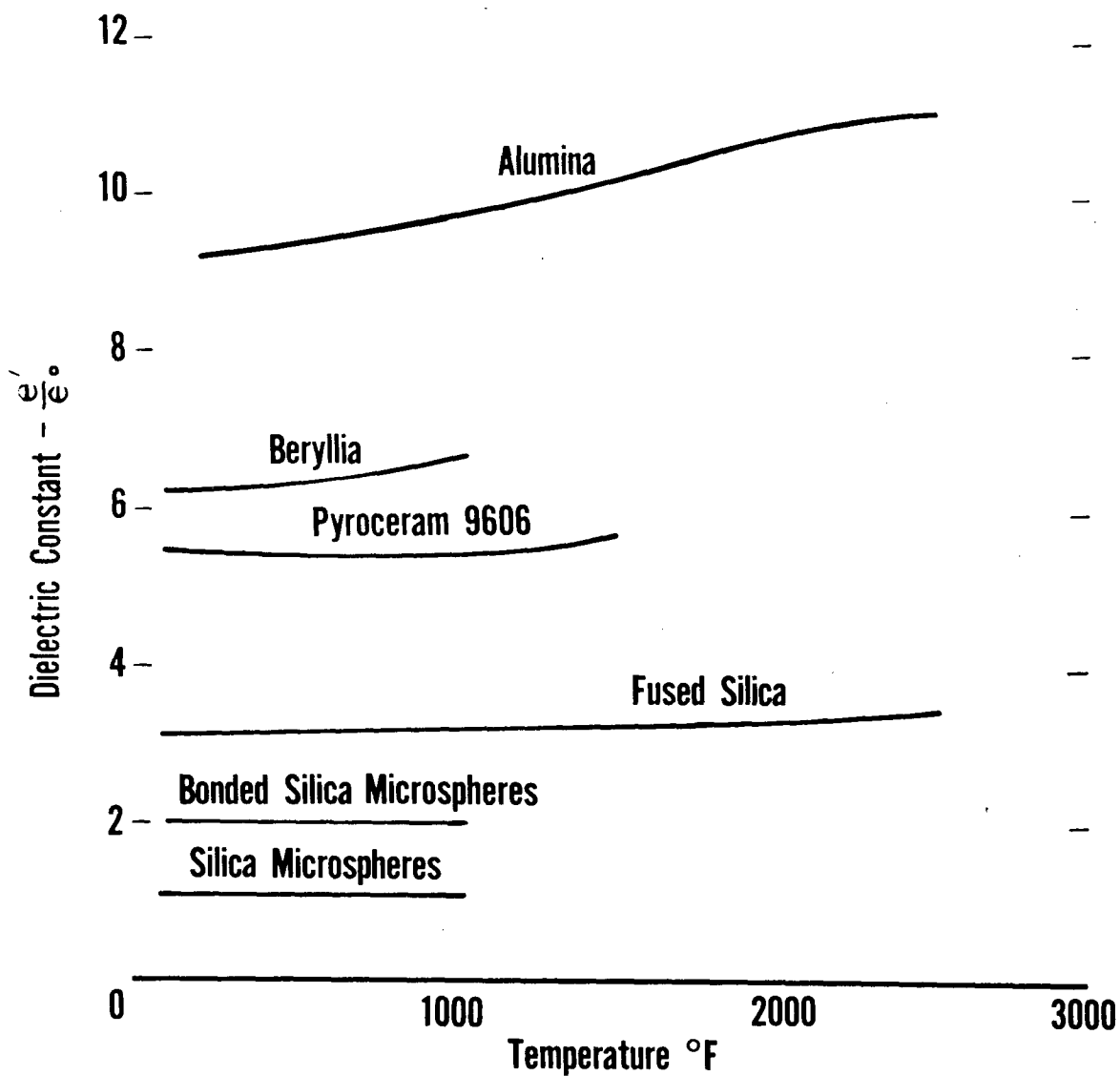


Figure 4.

INFLUENCE OF IMPURITY IONS ON TAN δ (500°C, 10⁶ C.P.S.)

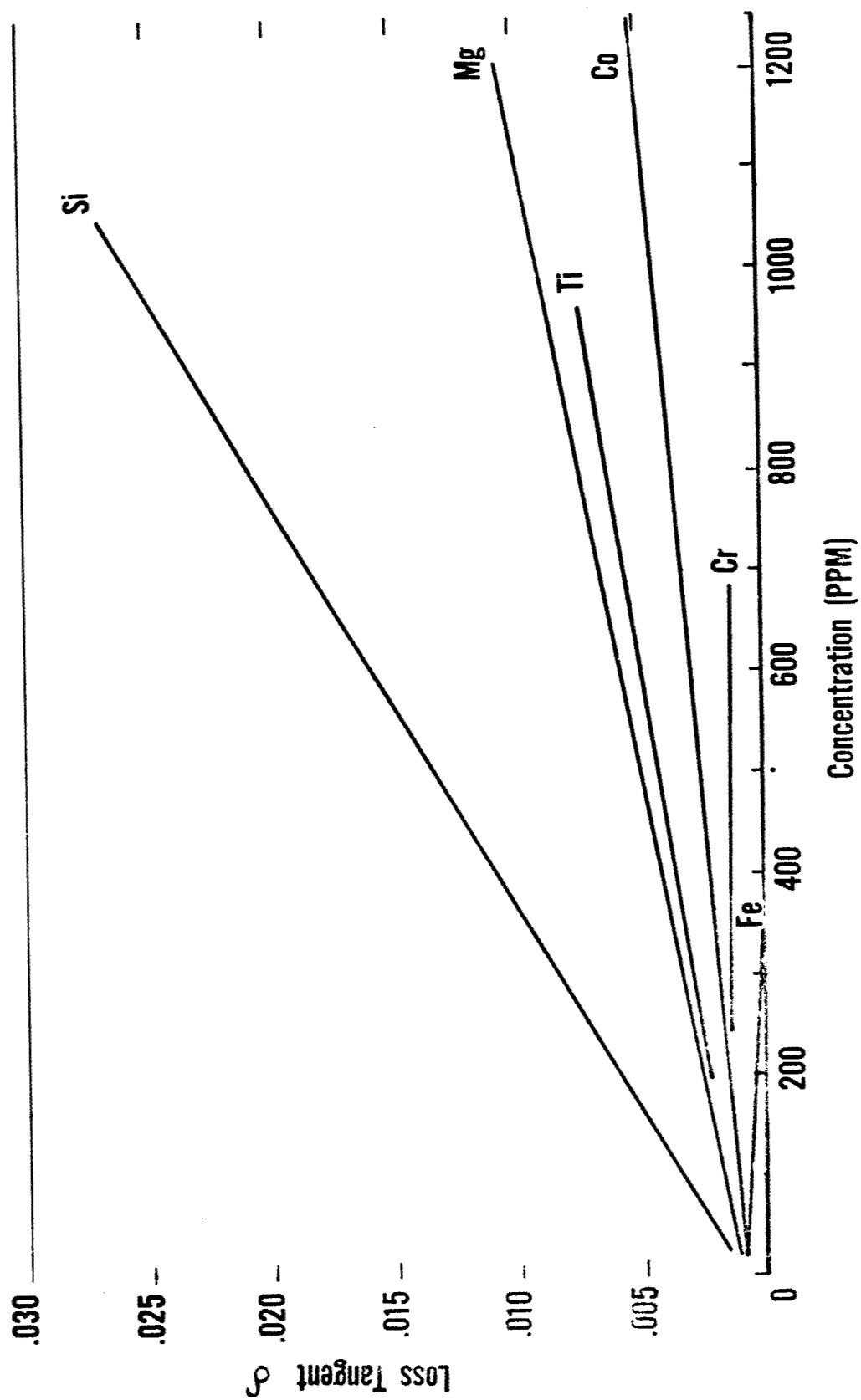


Figure 5.

SOME ASPECTS OF NEW POLYMERS FOR DIELECTRICS

Dr. G.F.L. Ehlers

Directorate of Materials and Processes, ASD

The Air Force requirements for new materials, and new electric or dielectric materials, are imposed to a great extent by the higher speeds of current and future weapon systems. This, together with the need to miniaturize equipment, means in most cases higher ambient temperatures for dielectric materials.

A wide variety of dielectric materials are already available covering not only the most diversified applications such as radomes, wire and cable insulation, capacitor dielectrics, potting materials, interlayers, etc. but also wide temperature ranges, from room temperature to far above 400°F for continuous operation over at least several years. This means even considerably higher temperatures for short-time applications. While most of the conventional organic polymers are applicable to temperatures up to about 300°F for continuous use, the silicone resins and rubbers are presently the only materials to be flexible and resilient and to have thermal stabilities of 400 to 480°F for longer periods of time. Still higher temperatures for longer periods of time are only tolerated by materials like glass, quartz, mica, ceramics, and certain oxides. These materials, however, are not flexible and are difficult to form, modify, and machine. It would be of considerable value to find new materials, which approach the thermal stability of ceramics and related materials and at the same time have the mechanical properties of plastics or elastomers.

The electrical characteristics required are very different depending upon the application, and in certain cases the electrical properties of a dielectric material are even more or less unimportant. This is the case with certain applications of embedding resins, which possibly have to have flexibility, strength, moisture impermeability, but not necessarily superior dielectric properties. However, generally one or more of the following properties are required: stable dielectric constant (either high or low) over a temperature and/or frequency range of interest, low dielectric loss over temperature and/or frequency range of interest, high volume resistivity, and high dielectric strength.

Do we know how to accomplish these properties when synthesizing a new polymer? So far not too much knowledge has been accumulated to predict the dielectric properties of unknown chemical structures, (figure 1). One of the few things we are able to do is to predict the order of magnitude of the dielectric constant from the dipole concentration, which requires known data from related structures to first estimate the dipole moment of the unknown material. The dipole moment of a material depends upon the types of chemical groups or elements present in the molecule. The bond between each two elements in the molecule can be considered as an electrical dipole, and the product of the total positive or negative charge at the center of gravity by the distance between the centers of gravity is the dipole moment. Chemical groups with high and low dipole moments are known and can be introduced into a polymer to change its dielectric constant. Furthermore, the dielectric dispersion and the loss factor maximum is related to the second order transition point. The second order transition point is the temperature, at which, upon cooling, the substance converts to the glassy state and the microbrownian movement of chain segments ends, considering an observation or relaxation time of the order of 10^3 seconds. It is therefore a measure of rigidity in the structure, and the

second order transition temperature rises with the introduction of sterically rigid elements or with groups, which introduce strong secondary bonding forces. It can be seen from figure 1 that the dielectric relaxation temperatures measured at different frequencies can be extrapolated to the second order transition point at a frequency or relaxation time of 10^3 seconds. There is only a limited possibility, however, that the temperature of dielectric relaxation from the second order transition point can be predicted because the slopes of the curves are different. The second order transition point itself of a projected new structure can only be predicted when several polymers of a series are already known. At the second order transition point the rate of increase or decrease of a number of physical properties, and also of the resistivity, changes abruptly. This correlates the resistivity to the second order transition point, as can be seen under ρ , on figure 1 (cont'd).

Other than these correlations, there is only a very crude relationship among the dielectric data themselves: low overall loss generally means high resistivity and high dielectric strength.

Besides the limited knowledge about correlations between structure and dielectric properties, we are often not free to establish the dielectric properties we want, for instance, low polarity, because polar groups are often needed to obtain good physical properties.

It is felt, therefore, that in the early stages of the development of a material the dielectric properties play a secondary role and that emphasis should be directed towards thermal stability. This has already been pointed out by Dr. Evans at the Dallas Meeting in 1958 and is still valid. Fortunately, we know much more about promising structures for thermal stability than for good dielectric properties. Here, however, considerable difficulties are involved with the synthesis of the desired structures.

Figure 2 shows a number of structures which we would consider promising for thermally stable polymers. Novel inorganic structures include the Si-N, Al-O, and P-N backbone, while favorable organic structures contain aromatic, cycloaliphatic, and heterocyclic systems, or conjugated double bonds. A majority of these structures have been synthesized already; however, most of these are of rather low molecular weight, which means that the mechanical properties are also low. We have to find new procedures to raise the molecular weight of these structures to obtain materials for practical applications. The thermal stability of these novel polymers, however, is very promising. Figure 3 represents weight loss curves obtained in the thermobalance. In the thermobalance, a sample of the material is heated increasing the temperature at a constant rate, in this case $150^\circ \text{C}/\text{hour}$, under nitrogen. The weight loss of the material is an indication of its stability against degradation. The figure shows the weight loss curves of the two most stable conventional polymers, a polysiloxane, and polytetrafluoroethylene, compared with one of the most promising novel polymers, a polybenzimidazole (a pure organic structure).

We do not know anything about the dielectric constant, loss, and resistivity of these new polymers. The reason is that most of the structures have been developed only recently, or have not been obtained in optimal purity. Furthermore, we had no reliable method so far to obtain reliable and reproducible dielectric measurements from small amounts of powdery materials. Recently however, under Air Force contract, procedure and electrodes for the determination of dielectric constant, dielectric loss and resistivity in

temperature and frequency dependence of experimental materials have been developed. Powders are compacted in special cells under pressures of 15,000 to 18,000 psi and the electrical measurements carried out by using painted silver, circular electrodes. Temperature ranges are between room temperature and approximately 400°F, the frequency range between 60 cycles and 1 megacycle.

The outcome of the testing of some of the experimental materials will be of considerable interest. There are indications to assume that some of the organic structures shown on figure 2 are semiconductors rather than insulators. According to the present theories, aromatic structures such as the benzene ring and conjugated systems of double bonds permit shifting of electrons from place to place and should therefore be conducting, provided that a path exists to move electrons from one ring or chain to the next. The fused ring structure of graphite is a good example for this principle. It is therefore possible, that structures of prevailing aromatic or conjugated structure, and perhaps also organometallic polymers, are potential semiconductors, and that we might find novel insulating materials preferably in the field of inorganic polymers. However, it is too early to make predictions.

What we need for the near future (and this is part of our present research program) is (a) to synthesize novel, thermally stable polymeric structures and (b) to collect data of dielectric properties of these experimental materials, to establish a better background on structure-property relationships.

CORRELATION BETWEEN STRUCTURE and DIELECTRIC PROPERTIES , (1)

- High Dielectric Constant = High Dipole Concentration
Low Dielectric Constant = Low Dipole Concentration
- Dielectric Relaxation (o) And Second Order Transition Point (x)

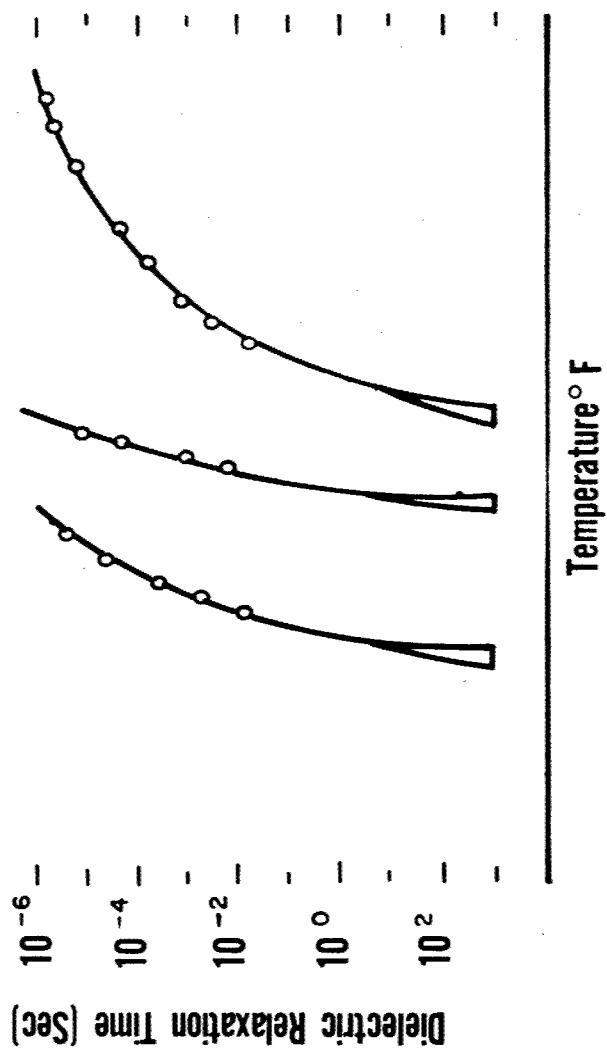
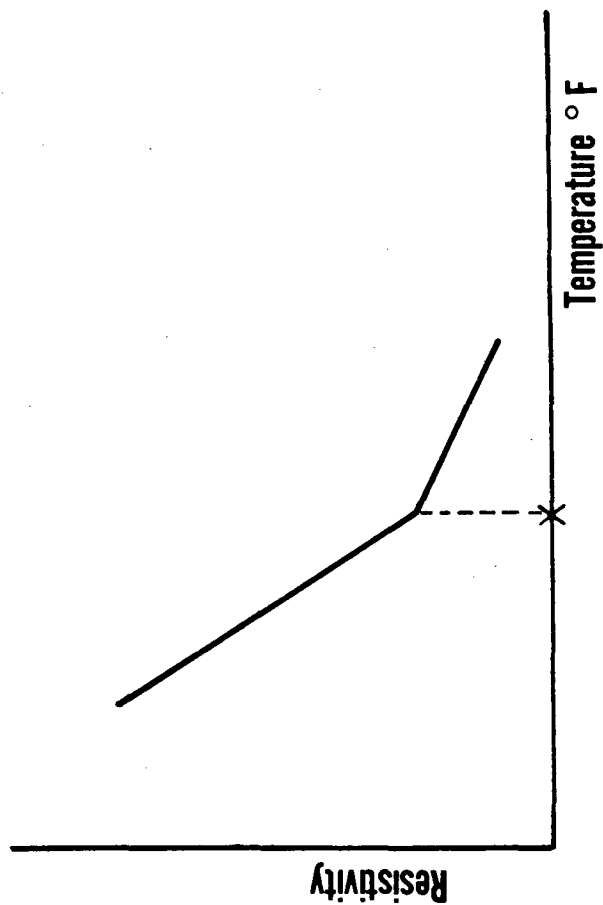


Figure 1.

CORRELATION BETWEEN STRUCTURE and DIELECTRIC PROPERTIES, (2)

- Resistivity And Second Order Transition Point (x)



- Low Loss High Resistivity High Dielectric Strength
- High Loss Low Resisting Low Dielectric Strength

Figure 1. (Cont'd)

THERMOGRAVIMETRICAL ANALYSIS of CONVENTIONAL and EXPERIMENTAL POLYMERS

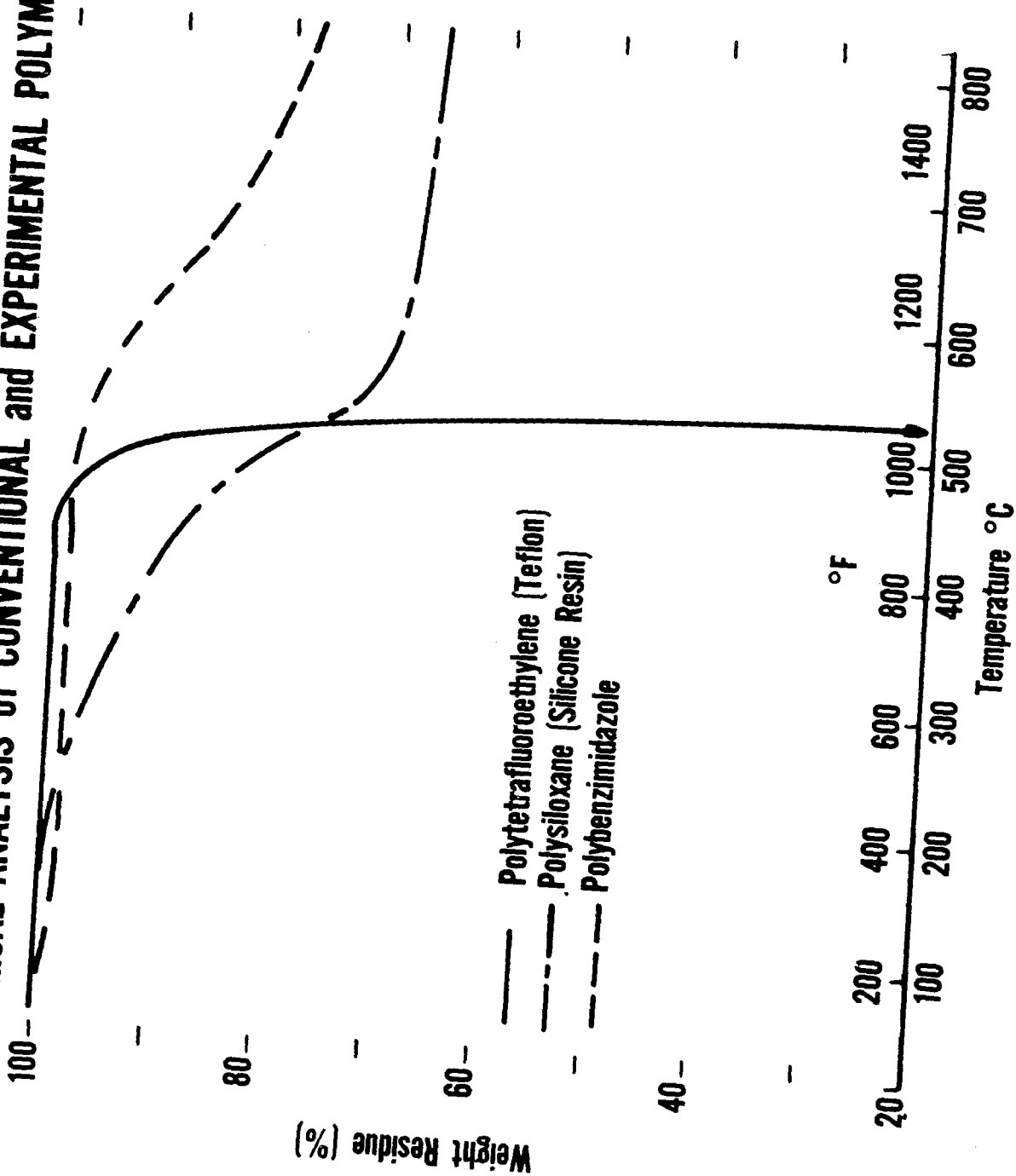


Figure 3.

PROGRESS ON THE RESEARCH OF SOLID STATE PHENOMENA AND MATERIALS

Captain William Metscher

Directorate of Avionics, ASD

Introduction

The field of molecular electronics will, without doubt, tax the technical abilities of both scientists and engineers in an effort to relate the multitude of solid state phenomena with the many necessary circuit functions. To clarify any misinterpretation of the words "Molecular Electronics" let the following serve as a definition for the purpose of this paper: The molecular electronics concept implies a composite electronic circuit which utilizes the intrinsic properties of atoms and molecules in the solid state (both individually and in combination) for the performance of complete circuit functions.

Before utilization of solid state phenomena for the performance of circuit functions can be realized, it will be necessary to satisfy certain fundamental requirements. To state these requirements involves only some logical thinking; the fulfillment will come only after much future effort. These requirements are considered to be the following; (1) the available solid state phenomena must be well understood, (2) a classification scheme permitting rapid reference must be developed, (3) mathematical techniques must be developed which will permit synthesizing molecular circuits, and (4) relationships between phenomena and function must be obtained.

The Electronic Technology Laboratory at the Aeronautical Systems Division, formerly the Wright Air Development Division, has a dual purpose basic research program in progress to spearhead realization of the concept of molecular electronics. The first goal is to understand and classify solid state phenomena; the second is to mathematically relate phenomena to circuit functions. This basic research program is directed by the Advanced Techniques Branch of the Electronic Technology Laboratory in such a manner that the contractual efforts are designed to complement in-the-house research tasks. The Georgia Institute of Technology, under contract to the Electronic Technology Laboratory, is assisting in a survey and study of the known solid state phenomena. Two reports (1,2) on this survey, currently being printed at the Aeronautical Systems Division, will provide a first attempt at compiling a partial handbook of solid state phenomena. Related studies sponsored by Electronic Technology Laboratory at the University of Pennsylvania and the University of Michigan are also in support of the molecular electronics program. Another program sponsored by Electronic Technology Laboratory at the Catholic University of America will also be briefly mentioned because of some very significant results recently attained by Prof. C. F. Pulvari of that University. Progress on these programs as well as related in-house efforts will be discussed in this paper.

Although desirable, it is not to be implied that these efforts provide a panacea for all the problems encountered, or to be encountered, in the molecular electronics program. Rather they are designed to provide the basic research that will permit us to take that giant step down the road to truly new, effective, and efficient electronic systems.

Classification

The program at the Georgia Institute of Technology is designed to provide a summary of physical phenomena related to the solid state of materials. One of the goals of the study

is to gather together into a single source the physical phenomena pertinent to the solid state field. The second and concurrent goal is to devise a classification system which will focus attention on possible undiscovered phenomena and which will enable a design engineer to obtain the phenomena information he needs in a useful form, one in which he is not required to conduct literature surveys each time a circuit function problem arises. To date, only a general classification scheme has been formulated from this program. The approach has been the division of phenomena into three broad groups and then the subdivision of these groups into subgroups containing specific phenomena.

Group I includes those effects which depend upon the transport of electrons and holes and those which are intimately associated with band structure. Examples of subgroups in Group I would be (a) Galvanomagnetic and Thermomagnetic effects, (b) Semiconductor effects, (c) Electron Emission Phenomena, and (d) Energy Band Phenomena. Typical phenomena under these subgroups would be, for (a) Hall Effect, for (b) Conductivity Modulation, for (c) Photoelectric Emission and, for (d) Cyclotron Resonance. Group II concerns those effects primarily related to the dielectric properties of materials and transport phenomena for particles other than electrons and holes. Some examples of Group II subgroups would be (a) Mechanical Effects, (b) Optical Effects, and (c) Transport Phenomena. Typical phenomena that would be discussed under these subgroups would be; under (a) Magnetostriction, under (b) Faraday Effect, and under (c) Exciton Transport. Group III includes resonance effects, that is, effects which can be described in terms of discrete energy levels rather than energy bands. Possible subgroups of Group III would be (a) Resonance Effects and (b) Special Devices. Typical phenomena listings under these subgroups would be, for (a) Nuclear magnetic resonance and, for (b) Maser action. The reports soon to be released will contain 63 solid state phenomena in a format which includes a definition, a qualitative explanation, a mathematical description where possible, an indication of the magnitude of the effect, special interesting features, and an annotated bibliography. It is hoped that the wide dissemination of these reports will spur others in the field to investigate possible classification systems.

Another approach to the classification problem was developed within the Electronic Technology Laboratory by R. D. Larson and J. M. Blasingame (3) who indexed some 147 phenomena using a rectangular coordinate system. This system labels the positive portion of the X, Y, and Z axes with appropriate input or output information. The X and Y axes were inputs and the Z axis outputs. For a particular circuit problem an engineer would look on the X-Y axes for the available inputs and compare these with possible output information obtained from the Z coordinate. The intersection would be a cube containing a listing of phenomena having the features originally compared. The engineer then would use appropriate texts for detailed phenomena information.

A third approach being considered at Electronic Technology Laboratory by the author is the development of a "slide-rule of phenomena" which would facilitate finding rapidly certain information about known phenomena and possible relationships between phenomena. This approach requires a logical and sensible use of symbols so that related effects such as the Nernst and Ettinghausen - Nernst Effect will be clearly evident. Much work remains to be done since it is uncertain at the moment if sufficient information can be displayed in a "slide-rule" manner.

There are definite differences between the two classification systems previously mentioned and both have certain inherent short comings. These will be mentioned not to criticize but to point out some of the problems involved in devising a usable system. First of all under the Group-Subgroup System, effects such as the Hall effect, and the Righi-Leduc effect would be grouped together since they fall in the category of Galvanomagnetic and

Thermomagnetic effects. In the rectangular coordinate system they would not be grouped together since their outputs are different (one is electric, the other thermal) and in this system it is the form of the output which determines the phenomena grouping. In addition, neither system currently contains provision for including such effects as those caused by chemical adsorption and nuclear radiation both of which could constitute inputs to a particular system. For example, surface effects on certain junction devices can account for a considerable change in electronic properties (4,5). Chemical adsorption, nuclear radiation phenomena and other presently unclassified phenomena create problems because their effects on a completed system or when used in materials processing may change the nature of the output of an existing phenomena or they may create new phenomena. It would be possible, of course, to keep adding new categories to both of these systems so that eventually all possibilities would be included. The shortcomings of the existing systems are fully realized by personnel in the field. The important point is that the ultimate goal is to devise a classification system which is more basic and more accurate than any existing now. The present systems provide some idea, at least, of the information which must be available from any finalized classification scheme.

Past successes on in-house programs as well as on contractual studies indicate that a good classification system must be based on such fundamental considerations as, the types of chemical bond involved, the interaction of electrons with the periodic lattice of the solid, the quantum mechanics and classical mechanics involved in dielectric polarization, and the fundamental relationships of magnetization in all its various forms, to mention just a few.

The extensive literature survey which so far has resulted in the classification (by one system or the other) of approximately 147 solid state phenomena is only the beginning of the job yet to be accomplished. There are several reasons for this. First of all, many of the phenomena applicable to the solid state were discovered at times when the scientific community was either unable or unready to utilize them. For example, the Peltier Effect was known long before there were suitable materials available for extensive application. The Seebeck Effect was known and used for some time, but lack of the proper materials kept efficiencies lower than desirable. The Nernst Effect is a reasonably familiar phenomena but it has yet to be put to any great use such as in the generation of electrical power.

There are many so-called lesser known phenomena about which comparatively little is known, that is, the specific phenomena is observable but the basic physical explanation is still lacking.

There are still many solid state phenomena which have never been extensively investigated but which show some particular promise for molecular electronics.

More intriguing still, is the possibility of discovering either new phenomena or new materials or both as the result of the intensive study of, and comparison between, various existing phenomena.

Phenomena and Materials

There have been some promising results even this early in our program. At Georgia Tech., Dr. Schiebner has uncovered the possibility of a new effect, the modulation of magnetic susceptibility by an electronic field. Evidence to date indicates that the effect should be observable in thin films of the transition metals and compounds. Some preliminary experiments are in progress to actually observe the effect. These experiments

involve the measurement of the change in frequency of an oscillator operating at about 9 megacycles when a nickel film is inserted into the coil of the tank circuit.

New materials have also been discovered as a result of the phenomena approach. Prof. C. F. Pulvari, mentioned above, has found a new group of materials exhibiting ferroelectric behavior (6). These materials are composed of two antiferroelectric materials and have been discovered in the mixed crystal of sodium-vanadate-niobate. These new materials have been named "ferrielectrics" because of their analogy with ferrimagnetic materials. The reader is referred to reference (8) for details. It is interesting to note that chemical analysis of these crystals has not yet been accomplished because no suitable solvent has been found. These crystals were even insoluble in hot hydrofluoric acid. The important point here is that the state of the art was advanced as the result of a specific phenomena investigation.

There is another example worthy of brief mention here because it incorporates the same considerations concerning the chemical bond, that we believe must also be the foundation of a good classification system. During an in-house study, an effort was made to deposit pyrolytically a thin film dielectric which would possess good stability at high temperature, a high breakdown voltage, and low neutron cross-section.

From the viewpoint of dielectric properties only, the materials considered were boron nitride, aluminum nitride and silicon nitride. However, from neutron cross-section data, the boron compound was eliminated from further consideration. The nitrides of aluminum and silicon have covalent bonding, that is, complete electron sharing which links all atoms together in the solid. Greater stability was predicted for these compounds because a larger number of bonds would have to be broken to effect rupture by voltage breakdown. Furthermore, theoretically, there should be no free conduction electrons available, at least until higher temperatures are reached, if the material has sufficient purity. From the values of standard free energy of formation of the compounds from their elements, it was predicted that silicon nitride would be the most stable of the three. Chemical resistance to attack by acids, water, and oxidation also supported the above conclusions. As a result of this preliminary work, Barnes and Geesner (7,8) deposited pyrolytically thin adherent nonporous films of pure silicon nitride from the vapor phase on hot molybdenum substrates. These films maintained satisfactory dielectric properties to temperatures exceeding 600°C. As a protective coating, these films protected metal surfaces from atmospheric oxidation to temperatures exceeding 1000°C.

These are but a few examples of progress to date. They supply proof that the study of solid state phenomena is not only desirable but necessary. More important, they are helping us to pinpoint the most important basic physical considerations which must be used in the formation of a phenomena classification system. In contrast to the Georgia Tech. program mentioned earlier, the Electronic Technology Laboratory's program at the University of Pennsylvania under the direction of Prof. M. E. Caspari, is concerned with more specific phenomena and materials. This program was designed to contribute information necessary to understand more fully some of the basic physics involved in certain phenomena.

A brief discussion of some of the studies being conducted under this program may be of interest here. The immediate objectives of this program were: (1) to study the electrical properties of mercury atom aggregates, (2) to explore the Faraday rotation effect in semiconductor materials, (3) the investigation of new compounds that may have promising semiconductor properties, (4) certain properties of insulators, and (5) the determination of the physical properties of alkali halides, molecular crystals and magnetic

materials. The initial technical report (9) contained some very interesting preliminary results which are summarized in the following paragraphs.

The electrical behavior of gases such as mercury was expected to be of theoretical interest because the conduction process is closely related to that of impurity band conduction in semiconductors with the obvious exception that atoms in the gaseous state are more mobile. Experiments to date have not been successful because the conductivity of the quartz vessel containing the gas was found to be too large at the temperatures required to obtain a sufficient high density gas and this obscured the conduction in the gas. Suitable containers are presently being sought.

The Faraday rotation studies were performed to determine the effectiveness of using this technique to obtain information about the effective masses, relaxation times, and mobilities of the charge carriers in semiconductors. However, extremely pure crystals maintained at very low temperatures (e.g., liquid hydrogen, liquid helium, etc) are necessary because of the requirement that the mean free path of the carrier be sufficiently large to permit the observance of cyclotron resonance. Since it is not possible in all cases to prepare samples of sufficient purity for cyclotron resonance studies, it would be of value to know how much information could be obtained using a more convenient technique, such as Faraday rotation. Experiments conducted under this program demonstrate that specific information can be obtained about the effective masses, relaxation times and Hall mobility using the Faraday rotation technique. There are also indications that this technique can be applied to powdered samples.

Under the subject of new compounds, this program has yielded some very interesting data concerning the dissolution of alkali metals into the lattice of tungsten trioxide. In particular it was reported that silver tungsten trioxide is a semiconductor possessing a rather complex resistivity vs. temperature function. The aluminum borides which belong to the binary defect system, were found to have very high resistivities but behaved like impurity semiconductors.

The electrostrictive properties of oriented single crystals of rutile (TiO_2) were investigated. It was shown that rutile possesses one of the largest electrostrictive effects ever observed ($\approx 10^{-8} \frac{\text{cm}^2}{\text{Statvolt}^2}$) although it is not a piezoelectric crystal because of its centrosymmetric structure.

A new technical report (10) currently being printed will detail progress to date on the alkali-halides, molecular crystals and magnetic materials. This report will describe experiments on the alkali halides designed to yield information as to whether the ionization of excited F-centers by electric fields can be considered a Zener type tunneling or an impact ionization process. Of particular interest in the investigation of magnetic properties are the novel features designed into a Foner (10,11) type vibrating sample magnetometer. The revised design has yielded a device capable of controlling temperatures between 10°K and 600°K, yet is only 1/4-in. thick and 2-in. wide. This instrument is currently under test at the University of Pennsylvania. A torsion anisotropy apparatus will also be described in that report. Measurements of magnetocrystalline anisotropy are of interest since theoretical considerations permit the prediction of the relationship between anisotropy and magnetization as a function of temperature. Since there is little reliable data at low temperature, these studies are expected to add to a better understanding of low temperature-magnetic anisotropy.

Earlier in this paper, it was stated that mathematical techniques must be developed which will permit synthesizing molecular circuits. This is the ultimate goal of the work being sponsored at the University of Michigan under the direction of Dr. W. M. Brown. Although no reports on the project are available yet (12), there have been a few individual papers published (13,14). This program is intended to provide the mathematical foundations for the future utilization of physical phenomena for the performance of electronic circuit functions. It is the study of nonclassical circuit analysis and synthesis to describe the role of general circuit blocks in sensor and communication systems, and to mathematically characterize important classes of circuits which fall outside the scope of very restricted classical theory. Under consideration is the possibility of developing an operational theory for certain linear time invariant systems. Special problems of interest here are the application of operational methods to non-linear problems and the possibility of a general classification of the equivalence of certain non-linear problems to problems with time varying parameters. Since this program is relatively new, it will be sometime before any detailed reports are circulated. However, at the present time it appears that these mathematical studies will eventually help us in relating solid state phenomena with electronic circuit functions.

In-House Research

Because of the nature and goals of the molecular electronics program, the study of materials in thin film form is intimately related to all solid state phenomena studies. The Advanced Solid State Section, Advanced Techniques Branch of the Electronic Technology Laboratory has an energetic internal research program designed to add new knowledge to the field of thin film growth by the sputtering, vacuum evaporation, and pyrolytic deposition techniques.

Some mention has already been made of the pyrolytic deposition of silicon nitride (7,8). The ideal goal of our pyrolytic work under the direction of Dr. Barnes is eventually to be able to deposit any material desired on any substrate desired and to study the interface problems of multiple layer deposition. Several hundred materials have been deposited in thin film form and much of the information gained has enabled a less empirical approach to this technique. For example, the deposition of boron nitride films at relatively low temperatures (500°C). Previously, deposition of boron nitride thin films was accomplished at temperatures of the order of 1400°-1600°C which made it impossible to use certain substrates. The low temperature technique permits the use of many more substrate materials.

Sputtering and vacuum evaporation studies are under the direction of Dr. E. B. Henschke, who has contributed much new information to the interpretation of sputtering phenomena. Most notable has been the "Henschke Theory" which explains many of the sputtering phenomena heretofore not explained by existing theories. Ample references are listed for those interested (15,16,17,18,19).

Studies such as these will eventually enable the growth of new materials designed to display specific solid state phenomena for use in molecular electronics.

Conclusion

It is fully realized that the foregoing information covers a considerable range of interest. However, with the vast number of organizations now working toward the realization of molecular electronics, it is imperative that maximum communication be maintained between researchers in the field. The basic physical explanations of solid state phenomena

have really only been under serious study for approximately the last 15 years. Much work is yet to be accomplished since phenomena must be understood completely before a meaningful classification system can be formulated. If a successful classification system is developed then the last step of tying together phenomena and electric function should enable the realization of the molecular electric concept.

APPENDIX

The following addresses are listed for those who desire to obtain the references listed in the bibliography.

References Nos. 1, 2, 3, 9, and 10 can be obtained from:

Aeronautical Systems Division, ASRNEA,
ATTN: Mr. J. M. Blasingame, Wright-Patterson AFB, Ohio

References Nos. 4 and 5 can be obtained from:

The Institute of Technology, MCLI,
ATTN: Dr. W. C. Lehmann, Wright-Patterson AFB, Ohio

Reference No. 6 can be obtained from:

Prof. C. F. Pulvari, Electrical Engineering Dept.
Catholic University
Washington, D.C.

References Nos. 7 and 8 can be obtained from:

Aeronautical Systems Division, ASRNEA,
ATTN: Dr. C. R. Barnes, Wright-Patterson AFB, Ohio

Reference No. 12: Requests for future distribution of this report should be addressed to:

Aeronautical Systems Division, ASRNEA,
ATTN: Mr. G. R. Branner, Wright-Patterson AFB, Ohio

References Nos. 13 and 14: Submit requests directly to:

University of Michigan, Willow Run Laboratories,
ATTN: Dr. W. R. Brown, Ann Arbor, Michigan

References Nos. 15, 16, 17, 18, and 19 should be requested from:

Aeronautical Systems Division, ASRNEA,
ATTN: Dr. E. B. Henschke, Wright-Patterson AFB, Ohio

BIBLIOGRAPHY

1. Scheibner, E. J. and Bennett, A. L. - Research on Various Phenomena for the Performance of Circuit Functions. WADD Technical Report 59-737, October 1959. Aeronautical Systems Division, Wright-Patterson AFB, Ohio.
2. Scheibner, E. J. - Research on Various Phenomena for the Performance of Circuit Functions. WADD Technical Report 61-148, October 1960. Aeronautical Systems Division, Wright-Patterson AFB, Ohio.
3. Larson, R. D. and Blasingame, J. M. - "Phenomena of Interest to Molecular Electronics". AIEE Winter General Meeting, Jan 31 - 5 Feb 1960.
4. Metscher, W. - "Irradiation of P-N Junction Diodes". Institute of Technology, March 1957. Wright-Patterson AFB, Ohio.
5. Freyer, G. J., Metscher, W. and Lehmann, W. L. - "Gamma Irradiation of Germanium Diodes Under Controlled Ambients". Ohio Section of the American Physical Society, Antioch College, Yellow Springs, Ohio. - 23 April 1960.
6. Pulvari, C. F. - "Ferrielectricity". Physical Review, Vol. 120, No. 5, 1 December 1960.
7. Barnes, C. R. and Geesner, C. R. - "Silicon Nitride Thin Film Dielectric", Journal of the Electrochemical Society, Vol. 107, No. 2, February 1960.
8. Barnes, C. R. and Geesner, C. R. - "Silicon Nitride Dielectric" (2 patents) and "Improved Process for Depositing Thin Films of Silicon Nitride" (1 patent).
9. Caspari, M. E. - "Investigation of Physical Properties of Semiconductors", WADD Technical Report 59-549, April 1960. Aeronautical Systems Division, Wright-Patterson AFB, Ohio.
10. Caspari, M. E. - "Physical Properties of Insulators, Molecular Crystals, and Magnetic Materials" WADD Technical Report (To be published), December 1960. Aeronautical Systems Division, Wright-Patterson AFB, Ohio.
11. Foner, S. - Review Scientific Instruments, Vol. 30, 548 (1959).
12. Brown, W. M. - "The Analysis of Linear Time Invariant Systems" WADD Technical Report (to be published) Wright-Patterson AFB, Ohio.
13. Brown, W. M. and Palermo, C. J. - "Theory of Coherent Systems" (to be published in the IRE Transaction on Information Theory)
14. Brown, W. M. - "Area Transforms" - (to be published), Institute of Science and Technology, University of Michigan.
15. Henschke, E. B. - "Dynamics of Sputtering Phenomena" WADC Technical Note 55-474, June 1955, Aeronautical Systems Division, Wright-Patterson AFB, Ohio.

BIBLIOGRAPHY (Continued)

16. Henschke, E. B. - "Deposit Spot Patterns from Low-Index Planes of Metal Single Crystals in a New Theory of Cathode Sputtering" Journal of Applied Physics, Vol. 28, No. 5, April 1957.
17. Henschke, E. B. - "New Collision Theory of Cathode Sputtering of Metals at Low Ion Energies" Physical Review, Vol. 106, No. 4, 15 May 1957.
18. Henschke, E. B. - "Crystal Growth on Cathode Sputtered Copper Films by Pairs of Double Spiral Mechanisms Analogous to Frank-Read Sources". Journal of Applied Physics, Vol. 29, No. 10, October 1958.
19. Henschke, E. B. - "Collision Theories of Cathode Sputtering of Metals at Low Ion Energies". Physical Review, Vol. 121, No. 5, 1 March 1961.

REFRACTORY METALS AS ENGINEERING MATERIALS

Chairman	Mr. J. T. Gow
Speaker	Mr. T. D. Cooper
Panel Members	Mr. D. M. Forney, Jr.
	Mr. H. Middendorp
	Lt. L. Hjelm
	Mr. H. Black
	Lt. W. F. Payne

REFRACTORY METALS AS ENGINEERING MATERIALS

T. D. Cooper

Directorate of Materials and Processes, ASD

Introduction

The increasing need for materials able to perform at higher and higher temperatures for improved efficiency and for use in new systems has stimulated a great deal of effort directed toward the development of the refractory metals. Aerospace application for propulsion and re-entry, of course, has been the primary driving force. From a scientific standpoint, the body-centered-cubic refractory metals have presented a challenge which the research community has been eager to accept. Their problems and behavior are of such an interesting nature that knowledge gained from studying them is, in itself, stimulus for more work.

Although there are a number of metals that can be considered as refractory metals by nature of their high melting points, the four of primary interest are columbium, molybdenum, tantalum, and tungsten. The high melting platinum group, iridium, osmium, ruthenium, as well as rhenium (Re), have melting points above 4000°F, but have only limited availability. Consequently, the discussion will be limited primarily to the first group, Cb, Mo, Ta, and W.

These metals have certain properties and characteristics that are similar in nature to each other. Some of their physical properties are shown in figure 1. They are all characterized by high melting points, ranging from Cb's 4474°F to W's 6170°F. Also, as their melting point increases, so does their density, from Cb's 8.6 gm/cc (which is a density of little more than iron base alloys) to W's very heavy 19.3.

Not to be overlooked is that utilization of the higher melting points exacts its price--the burden of greater weight. The importance of this fact cannot be overemphasized when considering aerospace applications, since structural weight has become significantly more important than ever before. Because of this fact, higher density metals must be used sparingly and only where their own unique combination of strength at high temperatures, or their high melting points, or other special properties will completely justify paying the penalty.

Applications

Applications of the refractory metals in currently operating systems can be reviewed rapidly, for they are very limited at the present time. They have several uses in a variety of electronic applications, in tubes, condensers, etc., but these will not be discussed in this presentation. Mo and W are being used in propulsion systems even now, particularly in solid fueled rocket nozzle and vector control applications, but the bulk of the applications for these materials is still ahead, some in the rapidly approaching future. The primary uses will be in two major areas, structure and propulsion. A third area of consideration which is just as important, although somewhat farther away in the time cycle, is the generation of power, such as electrical energy, in outer space.

In propulsion applications, summarized in figure 2, refractory metals will be used in all major devices, solid and liquid rockets, nuclear propulsion devices and high perform-

ance air breathing devices such as ramjet engines. In solid rocket applications, the most interest as far as refractory metals are concerned is centered about W or possibly suitable W alloys which will be an important part of the materials system comprising the nozzle area and vectoring devices. Whether it will be used in the form of thin wrought sheet to minimize weight, or a plasma sprayed product, or a more massive form which will accommodate a cooling technique by infiltrating with copper or a refractory oxide will depend upon the particular system and upon later developments in this area. The primary advantage of W for these applications is its high melting point. Its resistance to erosion and thermal shock is also very good when compared to other available materials. The drawback is its weight, and designs will undoubtedly incorporate only the amount necessary to do the job. Therefore, developments for this application have been to a great extent in the area of fabrication of W in attempts to obtain a suitable geometry.

There has been recent interest in small, uncooled liquid rockets, primarily for directional control uses. Interest here seems to be in Ta base alloys because of their high melting point and good fabricability. Nuclear propulsion systems such as the nuclear ramjet (Project Pluto) and the nuclear rocket engine (Project Rover) will have a number of requirements for high temperature materials up to 4000°F such as supporting material for fuel elements. In ion-propulsion units, the work function of W in the temperature range 2000° to 2500°F seems to be well suited for the ionizing surface and other refractory metals, such as Cb or Mo which will be used to contain the liquid and gaseous cesium. Ramjets will utilize refractory metals for resistance to aerodynamic heating encountered as a result of their high speed in the atmosphere.

The application which has been instrumental in stimulating effort for refractory metal development is in re-entry vehicle structural requirements, which encompass a variety of problems. Re-entering the earth's atmosphere from orbital or super-orbital flight, requires large quantities of energy to be dissipated in the form of heat. Re-entry in a controlled manner, as opposed to the ballistic re-entry of an ICBM or the semi-ballistic re-entry of the Project Mercury capsule, has precipitated proposals of a number of structural methods for use in constructing lifting vehicles. It is in these structures that many materials challenges exist, and where refractory metals will find use. Examples of two types of proposed radiation cooled re-entry lifting vehicles, a lifting body type and a glider type, are shown in the next two figures. Figure 3, a lifting body, is a refinement of the semi-ballistic type. This type vehicle consists primarily of fuselage, with wing loading of approximately 40 lbs/ft² or higher. A second type, figure 4, is a glider which has a higher lift-to-drag ratio, more wing area, and, consequently, lower wing loadings than the first. This type expends much more of its energy at higher altitudes and consequently has lower structural re-entry temperatures than the lifting body type. The equilibrium surface temperatures expected in these types of vehicles are given in figure 5 for both orbital and super-orbital re-entry. Time periods involved are from 25 to 90 minutes. The actual material temperatures will be somewhat lower than these, and will also be dependent upon such factors as sweep angle, wing loading, edge radii, and emissivity, but the requirements for structural materials should be evident. Cb and Mo alloys will find use in the lower temperature range shown, with Mo and perhaps Ta alloys competing in the intermediate range. In the higher range, W and its alloys will have to compete with graphite, ceramics, and other high temperature materials or systems. The requirement for refractory metals in these applications will be in the wrought condition, and primarily in the form of sheet. This is particularly true in radiation cooled structures, where a heat resistant shell is used to protect the load carrying substructure. Consequently the most urgent need for material for these applications is not for high strength sheet material,

but for high quality sheet material, with consistent and reproducible properties and, of course, suitable protective coatings.

The third broad area of application is in the generation of power in space. Large quantities of electrical energy will be required to operate low-thrust propulsion devices in space, such as in ion-propulsion and plasma propulsion units, for long periods of time. One approach to generating this electrical energy, the system shown in figure 6, is by use of a nuclear reactor, transferring the heat energy to a turbine-generator combination by use of liquid metals. Refractory alloys, and particularly those of Cb alloys appear to be ideally suited for such an application, for containing liquid metals like sodium and potassium. There will further be a requirement for turbine materials that will not be exposed to oxidizing environments for which refractory alloys should be ideally suited. Boiler and radiator materials are needed in these systems for transferring heat from the liquid metals to the working fluid. In these applications, very long transfer periods, e.g., (10,000 hrs) are required. Unfortunately, data of this nature does not yet exist for the refractory metals.

There are many other uses where refractory metals have potentialities, and it seems very likely that more and more applications will appear as systems are further improved and as the refractory metals themselves are developed.

State of the Art

The important task now, however, is to bring the refractory metals as rapidly as possible to the status of truly engineering materials so that they may be applied with confidence to aerospace projects, whose success is dependent upon them. At an accelerated rate efforts have been expended to appraise and develop the required metallurgical knowledge and production capability to infuse the refractory metals and their alloys in various mill product forms with useful, reliable, and reproducible engineering properties.

The present state of the art for the refractory metals has grown considerably, so that a detailed review of the total effort would far exceed the time available. In fact, a recent DMIC document summarizing only Government sponsored projects related to the refractory metals lists 320 projects active since July 1959. However, a broad review will serve to stimulate discussion concerning the problems surrounding refractory metals and solution of these problems.

In assessing in a qualitative manner the overall stage of development of the refractory metals today, there are some general comments that can be made concerning the kind of work in progress. Needs of the effort have been developmental, in nature, attempting to solve the many practical problems associated with manufacturing useful refractory alloys and fabricating them to the desired shapes. As a result, there has been less emphasis on fundamental research. Recognizing this tendency, the Air Force has devoted a sizeable portion of its refractory metal program to support fundamental research to learn more about the mechanisms of flow and fracture recovery, recrystallization, and, in general, the physical metallurgy of these metals. This will provide the technological basis for the further growth of the refractory metals.

There has been no great problem as yet in the development of alloys that will provide the strength at temperature needed for currently anticipated systems. There is, of course, a constant effort to try to improve these alloys to get a better combination of other properties in addition to strength, such as low temperature ductility. At present, the state of the art seems to be ahead of the applications as far as identifying usefully strong alloys

is concerned. However, before these alloys can be translated from the laboratory into useful material for weapons systems, they must be appropriately fabricated. At present there is a shortage of suitable production facilities for providing refractory metals in the wrought forms needed both for evaluation and for use. Because of this limitation much of the production development work and, indeed, some of the thinking, is handicapped because of the tendency to make refractory metals production technology suit the existing equipment, which was designed and built for the production of steel and other less difficult-to-handle metals. While this may be desirable from an economic standpoint, it may not solve the problem. Reproducibility and consistency have not been obtained in the refractory metal mill products that have been produced to date. If the material needs for planned weapons systems are to be met, this problem must be faced and perhaps both the equipment and the thinking changed. More is being learned concerning the importance of processing and processing sequence on the properties of wrought refractory metals. If we are to take advantage of this knowledge, adequate processing facilities will be required.

Several basic problems must be solved to make the refractory metals engineering materials for almost any application, whether it be related to military uses or not, and these are the problems discussed in this paper.

Refractory Metal Properties Problems

There are three general categories which have emerged as the major stumbling blocks to progress: (1) poor oxidation resistance, (2) low temperature brittleness, and (3) consolidation and fabrication difficulties. The third problem is to a certain extent, a result of the combination of the first two mentioned.

The poor oxidation resistance of the refractory metals is well-known. All four of the refractory metals unfortunately have little or no resistance to it in the temperature range where their properties are needed for service applications. Alloy development efforts to alleviate this situation have not been successful. Because of this, a very large share of the effort being expended to make them engineering materials has necessarily been devoted to the development of suitable protective coatings. The degree of success achieved in this endeavor will determine the extent of the applications for which these metals can be utilized. Due to its major importance, this is the subject of another presentation and will not be discussed here, except to emphasize that it is the most difficult problem to be solved, particularly for service above 3000°F.

Related to the oxidation problem is the transition temperature, which is the temperature below which fracture occurs with little or no plastic deformation. The existence of the ductile-brittle transition temperature in the refractory metals has been recognized for some time. The transition temperatures for unalloyed, recrystallized refractory metals are shown in figure 7, as represented by changes in reduction in area in tensile tests as a function of temperature. The temperature or temperature range over which the transition occurs is a function of material and testing conditions, including: microstructure, grain size, grain shape; degree of strain hardening; strain rate; stress condition; and, composition, interstitial content, and substitutional content. The last variable mentioned, composition, deserves further comment.

In general, the effects of interstitial elements on transition temperature are being rather widely investigated. Interstitial content has been shown to have a less significant effect on this parameter in Cb and Ta than in Mo and W. The effect of substitutional additions has also been investigated, although not as extensively as interstitial effects.

Recent data generated by Begley and co-workers on the effect of substitutional addition to Cb are shown in figure 8. Here, the addition of group IVa elements, titanium (Ti), hafnium (Hf), and zirconium (Zr) to this group Va elements, Cb and Ta, have, based upon atomic weight percent additions, less pronounced effect on the transition temperature than do the group VIa elements, Mo, W, and chromium (Cr). Another interesting fact is the sharp increase in transition temperature resulting from the additions of Re. This is in contrast to the results reported by Battelle on the effects of Re additions to Mo and W, where the transition temperature is lowered by sufficient addition. So there are definitely effects from substitutional alloying additives on the transition temperature of refractory alloys, and more investigation of this area may be very helpful in guiding future alloy development efforts.

All four of the refractory metals crystallize in the body-centered-cubic structure and all exhibit a transition from ductile to brittle behavior. This transition temperature decreases from W to Mo to Cb, and although pure Ta is ductile at the lowest temperature tested, its yield strength increases rapidly as the temperature decreases, indicating that at low enough temperatures it will exhibit a transition. Implications as related to our objective of engineering refractory metal alloys are, of course, direct. The higher the temperature, the more severe are the problems that must be encountered—in forming, joining, and handling structures fabricated from these alloys—and the lower their reliability during service.

In contrast to the similarity noted among all four refractory metals, there are also certain characteristics inherent in the group Va metals, Cb and Ta, that differ from the VIa metals, W and Mo. The moduli of elasticity and the thermal conductivities of Cb and Ta are lower than Mo and W. The coefficients of thermal expansion of Cb and Ta are higher than those of Mo and W. Furthermore, the tolerances for interstitial and substitutional alloying additions are much greater in Cb and Ta than in Mo and W. Mo and W strain-harden more than Cb and Ta and, consequently, strengthening by cold working is more pronounced in Mo and W. But, we get back to similarities, when we compare elements of the same group; this is particularly noticeable in those aspects concerning alloying and processing, and was discovered during development of these materials.

Because of the low transition temperature of the base metal of Cb and Ta, it is likely that there will be many useful alloys whose transition temperature, in the recrystallized and as-cast condition encountered in welded structures, will be below room temperature. Some have already been developed. Transition temperatures of recrystallized alloys of Mo and W, however, will be above room temperature, and joining processes such as fusion welding will result in material that has a high transition temperature, a condition in all alloys investigated with the exception of those containing sufficient Re.

Research efforts to investigate various aspects of brittleness include studies of the mechanisms of flow and fracture and the degree to which interstitials are involved. Of particular interest now is the effect that substructure has on the behavior of the refractory metals. Understanding the development of low-angle grain boundary networks, their interaction with interstitial elements, and their effect on recrystallization, yielding, and fracture at all temperatures should throw considerable light on the low temperature brittleness problem. Many problems have not been resolved, such as why varying degrees of cold working in the group VIa elements, Cr, Mo, and W, results in a fiber condition which lowers their transition temperatures. There are also questions concerning fracture itself, such as where it initiates, how it propagates, and what part interstitial elements and twinning have in this process.

Processing Problems

Primary consolidation of the refractory metals has been accomplished principally by one of two methods, by powder metallurgy, or by melting methods, such as arc-melting or electron-beam melting. The powder method is the oldest technique and has been applied primarily to W, Ta, and Mo. The development of melting methods considerably increased the range of alloy compositions and the sizes of ingots that can be prepared, and these methods are now being widely used for consolidation of all refractory metals.

Appreciable purification of the metal can be obtained by vacuum melting by volatilization of impurities, particularly in the case of electron-beam melting of Cb and Ta. Oxygen (O) can further be reduced by adding suitable deoxidizers, such as carbon (C), to the melt.

The breakdown of the generally large-grained ingots resulting from the melting processes is a challenging problem, particularly for the more intractable high strength alloys. The best solution to date has employed the hot extrusion process, particularly since the development of improved glass lubricating and die coating techniques. Forging is also being used, both for primary breakdown of more fabricable alloys and for further working of extruded billets. The general procedure in making sheet product is hot rolling, with suitable intermediate anneals, until the material is sufficiently worked to allow finishing at some lower temperature. If other wrought forms, such as extrusions or forgings are desired, a suitable processing course in that direction is followed. Powder metallurgy techniques are also used for this primary consolidation by pressing, sintering, and further fabricating to mill product forms. The powder process is used as one method of preparing electrodes for arc melting.

Since details of these processes are being discussed by another panel, our comments will be limited to some of the problems associated with the processes.

The problem of oxidation has already been pointed out and, of course, is important in processing because of the high temperatures required for working the refractory metals. Mo and W are traditionally heated in hydrogen atmospheres to prevent oxidation since the solubility of hydrogen (H) in these metals is lower and there is no hydride formation. Although the question has been raised as to whether this is truly an inert atmosphere, there are no apparent reactions to indicate the contrary. Gas fired furnaces with reducing atmospheres are also used. Hydrogen-containing atmospheres cannot be used with Cb and Ta, for large amounts of the interstitials, H, nitrogen (N), and oxygen will dissolve in and embrittle these metals.

Processing of Mo and W is often accomplished in air. The oxides of these metals are volatile, Mo above 1800° and W above 2300°F, and material will vaporize, but the solubility of interstitials is generally low. There is, however, a thin but undesirable surface contamination layer formed which must often be planed by grinding. Cb and Ta cannot be processed in air above about 1000°F. Unalloyed Cb and Ta of commercial purity can be processed at temperatures below this, but many higher strength alloys of Cb and Ta require hot breakdown, and this must be accomplished in inert atmosphere, such as highly purified argon or vacuum. Techniques of canning in Mo, Ti, or stainless steel have also been used, but this is an expensive, not always reliable, and generally undesirable method, particularly for large-scale production. There are some processing coatings that are being used that seem to minimize surface oxidation and contamination, but a certain amount of material must be sacrificed in subsequent scalping or pickling operations.

The value of processing refractory metals in completely inert atmosphere has many interesting possibilities which have not as yet been proved, although the current Infab facility may accomplish some of this. With such an atmosphere, not only can the effects of atmospheric impurities on resulting wrought products be eliminated but, perhaps more important, the opportunity to truly hot work the refractory metals will exist. A facility of this nature may eliminate many of the problems not attributed to processing.

Process Control

One of the most important aspects of any processing procedure used for the refractory metals will be control of the process. There are a number of processing factors that will most certainly affect the behavior of the wrought product. These factors are, for example, the temperature of deformation, the amount of deformation at a given temperature, the sequence of thermal and mechanical processes, and the times at temperatures during processing. The thermally activated mechanisms, such as recrystallization, recovery and polygonization, that will be operative during the warm and hot working operations can definitely affect the properties of wrought products. In addition, it has already been very clearly shown that many alloys will be susceptible to solution heat treating and aging reactions, which also will occur during hot and warm working operations. Some aspects of both of these occurrences have already been investigated. Laboratory data has shown that, in some instances, great variations exist in property data on what is now the closest thing to production sheet available, perhaps as a result of variations in the processing operation from one sheet to another. So it is important to understand such things as the nature of substructure formation, its effect and how to control it, the kinetics of solution treating and aging in various alloys and then control the processing to minimize the deleterious effects and take advantage of the desirable effects.

Since the primary need for refractory metals for aerospace applications is in the wrought form, and particularly in the form of flat rolled sheet, a Materials Advisory Board Refractory Metal Sheet Rolling Panel has been established at the request of the Department of Defense. This panel, in cooperation with the Army, Navy, and Air Force, is reviewing the current efforts to produce refractory metal sheet, making recommendations concerning the programs and the need for further work. The organization of this panel is shown in figure 9. Various subpanels have been established to provide more detailed study and recommendations for certain aspects of the sheet rolling area. There are now four major programs being sponsored by the Air Force and the Navy intended to produce refractory metal sheet which are being followed by the panel. They include projects for the production of Mo alloy sheet, Cb alloy sheet, and two projects for W sheet, one using powder compacts and the other starting with arc cast material. The panel is also kept informed of related projects sponsored by the various military contracting agencies.

In addition to these sheet rolling activities there are also projects on forging of Mo, Cb, and W and extrusion of Mo, Cb, Ta, and W.

In discussing the difficulties facing the refractory metals producers and users, some of the more important aspects were mentioned. There are other problem areas, such as joining, both by thermal and mechanical methods, chemical analysis, machining, and fabrication of components which were not mentioned, but which, nevertheless, are significantly important in their own right and which require adequate developmental effort.

Alloy Development

The most extensive alloy development efforts have been directed toward Mo, dating back to original interest in its potentialities for use in turbine applications. Although never successfully utilized because suitable protective coatings had not been developed for the severe conditions involved, a great deal of valuable data was generated which actually assisted in later developments for all of the refractory metals. Development of W for use in filament applications predates Mo work by many years. However because of the competitive nature of this area, details of much of the work on W were not published and, until recently much of the technology of W processing could be almost classified as an art. Developments in Cb and Ta have been much more recent. The current state of alloy development of each of the four refractory metals will be considered separately.

Columbium Alloys

Of all of the refractory metals, there has been more industry support of alloy development in Cb in recent years than of any of the other three metals. Perhaps the biggest reason for this interest is because of its versatility which makes it competitive for a number of applications. Unalloyed Cb possesses several inherently useful properties. It is ductile, weldable, has excellent fabricability, low density (as compared to other refractory metals) and is not susceptible to low temperature notch sensitivity. By alloying, it can be made resistant to liquid metal corrosion, can be made to have improved oxidation resistance, and can be greatly strengthened for high temperature applications. The problem is that it is not always possible to achieve the desired combination of improvements through alloying without sacrificing some of the other desirable properties of Cb. For example, a high strength, oxidation resistant combination has not yet been found. Neither has anyone as yet achieved the excellent high temperature strength obtainable through alloying without sacrificing something in fabricability and weldability.

A great number of Cb alloy compositions have been identified within the last few years. In fact, more than thirty alloy compositions have been carried to the point of identification as potentially commercial alloys. Among these are included some alloys with improved oxidation resistance, some that retain Cb's fabricability, and others that have very good high temperature strength. The short time-at-temperature properties of some of what might be considered the first generation of Cb alloys are shown in figure 10. Their compositions are given in table 1. Alloys with better fabricability such as Cb-65, FS-82, and D-31, have lower strength properties at elevated temperatures. Meanwhile, the higher strength alloys, such as Cb-7, F-48, and D-41, are much more difficult to fabricate and their weldability has been reduced. Fabrication difficulties result from the fact that because of their better strength at higher temperatures, the initial breakdown of the large-grained arc-cast ingots must be accomplished at higher temperatures where oxidation and oxygen diffusion to form a hard, brittle layer occur more rapidly.

Emerging from these first generation alloys are two, which for various reasons, will be among the first commercially available Cb base sheet alloys. F-48, because of its higher strength, and D-31, because of its combination of fabrication, fair oxidation resistance, and reasonable strength, are the two alloys included in the current Cb sheet rolling program now in progress. Additional experience with F-48 was obtained as a result of its inclusion in an Air Force program to build a typical hot load carrying structure. These two alloys, along with the Cb-1 Zr alloy, a lower strength alloy which is also promising for liquid metal containment, the FS-82 alloy, and the unalloyed Cb, constitute what are currently the only commercially or semicommercially available Cb alloys in sheet form.

There is now in existence a second generation of Cb base alloys, some of which are shown in figure 11. The alloy selection subpanel of the Materials Advisory Board Refractory Metal Sheet Rolling Panel has recently reviewed the present Cb alloy development efforts of the producers of the country. Of the seven producers that had data to present, a total of 13 alloys were considered as possible candidates for a sheet rolling program to be sponsored by the Bureau of Naval Weapons. Emphasis has now been shifted from the high strength type of alloy to a more fabricable type where ease of fabrication and weldability are the important property considerations. Unfortunately, many of these alloys are in a fairly early stage of development and making a uniform comparison of properties is not entirely possible. There are variations in high temperature strength of these alloys. There are also variations in low temperature ductility and weldability. Considerably more data must still be determined; further work to develop the unique advantage of each is still in progress.

General trends in Cb alloy development indicate that those solid-solution additions which impart the most high temperature strength are the group VIa elements, Mo and W. Also, when added in sufficient quantity to appreciably strengthen, it is these elements that raise the transition temperature and adversely affect fabricability and weldability. Another potent strengthening mechanism characteristic of most of the high strength alloys, is the interaction between one of the reactive metals, Zr or Hf, and the interstitial elements, C, O, or perhaps, N, to form precipitates. These reactions are very effective in high temperature strengthening and are important to ductility after welding.

Tantalum Alloys

For the last year or so, Ta has been the dark horse of the refractory metals. It was bypassed as a base material in early refractory metal developments for three reasons. It is heavy, being only second to W in density. Unalloyed Ta has very low strength, both at ambient and elevated temperatures, and it is expensive because of the comparatively limited supply. Its principle advantages are its high melting point and its excellent low temperature ductility, but its oxidation resistance is no better than that of other refractory metals. Because of its ability to accept a large number of elements in solid solution, it appears to be a very good base for alloy development. Recent developments on Ta alloy study programs have shown that it is possible to greatly improve the high temperature strength of Ta by solid-solution alloying without sacrificing low temperature ductility. The result is that ease of fabricability plus weldability can be achieved while still maintaining good strength at temperature.

The data presented for most of these Ta alloys, unfortunately, are the results of only limited tests of laboratory size quantities of material. Larger size quantities of the more promising alloys are being processed currently, however. High temperature tensile data for some selected alloys are shown in figure 12. Some of the data plotted were determined in the recrystallized condition. Because they are apparently solid-solution strengthened alloys, excellent properties are obtained without strain-hardening, as can be noted by comparing data on recrystallized alloys with stress relieved alloy data.

The Ta-30Cb-7.5V alloy is particularly interesting and is worth discussing further as an indication of what can be achieved in Ta alloys. Its density is much lower than unalloyed Ta because of the 37 weight percent of less-dense alloy addition. Its strength-to-weight ratio is particularly attractive in the 2300° to 2900°F range. But, more than just strength at temperature, it offers the unique property of exhibiting 20 percent elongation in the recrystallized condition in a tensile test at -320°F. To produce this alloy on a commercial basis, it has been consumable-electrode arc melted and further processed to experimental

sheet. During the process, it was cold rolled from recrystallized 0.5-inch thick plate to 0.040-inch thickness with no intermediate anneals. After welding, its minimum bend radius at room temperature was approximately 1.5 T, which, by refractory metal standards, is excellent. This alloy must undergo additional testing to further verify its properties. The results to date, however, serve to illustrate the potentialities of alloys of this nature.

There is only one Ta base alloy that can be considered as a semicommercial sheet material at the present time. That is the Ta-10W alloy, which is also shown on figure 12. This material was initially emphasized as nozzle insert material for solid rocket application, but holds promise for structural applications.

It has also been shown qualitatively that the same strengthening effects by precipitation or dispersion of oxides and/or carbides of Ti, Zr, and Hf, that have been identified in Cb alloys can also be achieved in Ta. This data is preliminary and further work is necessary to determine the extent to which it can be used, but the accomplishments already achieved will probably aid in improving the creep and rupture properties of Ta alloys.

Molybdenum Alloys

During the past decade the primary objective of the major research efforts on Mo base alloys has been to increase the high temperature strength of the base metal and to study the effect of thermal and mechanical variables on the properties of these alloys. These programs have advanced the useful temperature range of Mo alloys. Alloys with an increased recrystallization temperature have been developed which are stronger in both short and long time properties, through the addition of elements which have promoted solid-solution strengthening, precipitation strengthening, and/or strain-hardening effects at elevated temperatures.

The most effective strengthening benefits have been derived from increased carbon contents in combination with relatively small amounts of Ti and Zr. A second important advancement in alloy development involves the substitution of W for part of the Mo, which increases the melting point of the alloy. The addition of small amounts of Cb has also been effective in increasing strength. The strength-temperature relationship for certain compositions are shown in figure 13.

Since Mo alloys rely to a great extent upon the increased strength resulting from strain hardening, the effects of alloy addition on recrystallization temperatures are very important, and increased recrystallization temperature has been an important objective of alloy development. To date, the highest recrystallization temperature attained has been in the Mo-1.25 Ti-0.3 Zr-0.15 C alloy, where a 1-hour exposure at 3400°F was required for complete recrystallization.

Currently, the Mo-0.5 Ti alloy is considered commercially available and is the prime candidate for use in construction of heat shields for re-entry glider type vehicles. The Mo-0.5 Ti-0.07 Zr (TZM) alloy is also nearing the stage of commercial availability and will probably replace the Mo-0.5 Ti alloy since it has a higher recrystallization temperature and better high temperature strength.

In addition to these commercial alloys there are a number of more experimental alloys under development that exhibit excellent high temperature strengths. Two of these alloys are also shown in figure 13. The Mo-1.67 Cb-0.49 Ti-0.3 Zr-0.31 C alloy shown has much higher strength at lower temperatures, and although displaced by the Mo-25.1 W-0.11 Zr alloy in actual strength at 2400°F, still appears better when the data is density compensated.

These compositions reportedly present no serious problems in preparation by vacuum-arccasting. They have not yet been produced and tested in sheet form, however. The success that has been attained to date in fabricating these higher strength compositions into the wrought condition for testing is largely attributable to recent progress made in the primary breakdown of arc cast ingots by the hot extrusion process, particularly since coating extrusion dies with refractory oxides were improved and glass lubricants were properly identified.

The relationship that exists between the C, Ti, and Zr contents in Mo base alloys is one of the very challenging areas for alloy research and one that has received a great deal of attention. It is combinations of these three elements that provide the basis for the highest strength Mo alloys through the formation of carbides. Although data has been generated indicating relative additions of these elements necessary to obtain improved strength, and the effects that solution treating and aging have on properties, considerable effort is still needed in this area. It is particularly important to determine carbon's role in the strengthening, since it adversely affects low temperature ductility. Once the quantitative functions of these additions and the kinetics of the heat treating are better understood, it should be possible to determine the extent to which tradeoffs between low temperature ductility and high temperature strength can be made.

Tungsten Alloys

Alloy developments of W have been of two types to date, those made by powder metallurgy techniques and those produced by consumable-electrode arc melting methods.

Included in the powder metallurgy group are unalloyed tungsten and tungsten to which small amounts of various doping agents, such as mixtures of alkaline oxides with silica or alumina, are added. The doping agents are added primarily to retard recrystallization and control the grain structure formed to give interlocking, rather than equiaxed grains. Their effect on strength is probably not significant other than the recrystallization effect. These alloys are commercial, but are available primarily as rod or wire for fabricating filaments. The use of doped powders for production of W sheet material is being investigated on one of the sheet programs mentioned previously.

There are some other additions to powder compacted W which have been investigated that affect high temperature strength. These include Thorium dioxide (ThO_2), which also serves as a doping agent, and Tantalum and tetra Boron Carbides (TaC and B_4C).

Arc melting is also being used to prepare alloys and is somewhat more versatile in that there are more alloy systems that can be processed by this method than by powder methods. Limitations are in the volatility of the addition, and in the additions, such as Titanium, Silicon, Cobalt, Iron, Vanadium, and Nickel, which are difficult to retain. Figure 14 presents some data on various alloys of W. Of the alloys shown here, the only one that can be considered as commercially available in sheet form at the present time is unalloyed W. The other data represent results of some very limited tests on laboratory size quantities of material.

Much interest is currently centered on the W-Mo series. Although no significant strengthening effect at temperatures above 4000°F over unalloyed W is noticed for most of the W-Mo alloys, the W-15 Mo, which seems to have maximum strength in the system, shows some superiority up to 4000°F . Mo additions have grain refinement effects that are beneficial in breakdown and machining operations. Small additions of Group Va

elements such as Cb and Ta have been shown to improve strength at 3000°F (figure 15). In fact, one of the highest data points recorded for any material at 3000°F, 60,000 psi, is a W alloy containing only 0.57 Cb. Data for other alloys in this composition range prepared by different processing techniques have not yet duplicated this strength, being in the 38,000 to 40,000 psi level. The strengthening mechanism operative has not yet been established, but it seems likely that it is related in part to the processing method used. Tests at higher temperatures were not performed on that particular lot of material, but other data suggest that the tensile strength would start to drop rapidly at higher temperatures.

Recent experimental data on the W-Ta-Mo-Cb alloy series has outlined a number of very interesting solid-solution alloys. One of these alloys W + 5.7 Mo + 5.7 Cb tested at 3000°F resulted in an ultimate strength of 62,000 psi. Other alloys in this series, which were essentially W and W-Ta base, gave strength levels above 50,000 psi. These alloys are being explored further, both from a fabricability standpoint and also for strength above 3000°F.

In general, alloy developments in W have been very limited. Many problems have been encountered in preparing W alloys, and testing capabilities at temperatures above 3000°F are limited. With the exception of the addition of the refractory metals to W, most alloys are dilute in nature and permit the advantage of strain hardening. At temperatures above 3000°F, where W will be competitive as a structural material, strain hardening will not be effective because of recrystallization, solid-solution strengthening will become less effective and, to get higher strengths, the addition of inert dispersed particles will probably be the most important strengthening method.

Fundamental Work

The importance of strong efforts in what can be considered fundamental work cannot be over emphasized. Problems to be overcome in the time available are such that empirical solutions will not be adequate.

A more thorough understanding of the mechanisms of flow and fracture at both low temperatures and high temperatures must be obtained for use in both processing and application. Although considerable effort is now underway concerning the effects of interstitials in the refractory metals on strain aging and other behavior, more work is needed, particularly on problems of interactions between interstitial elements and substitutional elements and their effect on strength and ductility. For coating applications and applications where dissimilar metals will come in contact, diffusion data are needed. A variety of physical properties must be determined at elevated temperatures such as thermal conductivity, heat capacity, thermal expansion, etc., particularly as new alloys emerge that seem to be suitable for particular applications.

Other Needs

Alloy development must necessarily be emphasized probably as long as refractory metals will be used. The efforts should be to achieve optimum combinations of strength at temperature combined with other properties for specific applications. The quest for alloy additions to Mo and W that will improve low temperature ductility must continue, for the obvious desirability of a weldable W or Mo alloy, which will only be achieved by this method. Related to alloy development is what appears to be one of the most interesting and perhaps fruitful areas for work and one which has not yet been very deeply explored—combining suitable alloy composition with proper heat treatment to give

improved properties. Of particular importance are the formation of carbides and oxides, and learning to control their shape and location in the matrix to combine strength with maximum ductility. It is also very important that much additional data be generated on alloys that have already been identified. Needed are data at elevated temperatures, particularly above 3000°F. There has been practically no compilation of fatigue data, including sonic fatigue. The same kind of data are needed for material systems, that is, refractory metal alloys with suitable protective coatings. Long time creep and rupture data up to 10,000 hours are needed. Much of this data on alloys can only be determined when processing procedures have been properly developed and suitable quantities of material produced. In fact, it does not seem unlikely that far more material will be consumed in testing in the near future than will be used in applications thereafter.

So far, many promising refractory metal alloys have emerged from the laboratory research efforts, although developments in Cb and Mo base alloys to date far exceed those in Ta and W. While the discussion has been centered upon comparisons of high temperature strength and particularly short time strength, we obviously do not intend to imply that alloy development efforts are or need to be based on this one criterion. Just as important to specific application will be the alloy's ability to be drawn into tubing or complex shape, or to be rolled to very thin sheet or foil, or its ability to be welded or brazed, or to withstand stresses for very long periods. This diversity requires that development of alloys of all four refractory metals be pursued rather than a concentrated effort on only one or two of them. Only in this way can suitable material be available to the designer to satisfy specific jobs.

There is apparently no aspect of refractory metals technology that can be neglected or where progress has been sufficient to date that more effort would not be justified. The problem is in assigning the correct priority to individual tasks and areas so that achievement of the goals of providing suitable high temperature materials can be attained in the shortest possible time.

The importance of processing the refractory metals has already been emphasized. The problem of getting wrought products of uniform and consistent properties, thickness, and flatness is currently second only to the coating problem as far as application of the refractory metals is concerned. It, therefore, must rank high as an area requiring continued effort. A better understanding of processing as related to microstructure properties, and effects of thermal treatments is needed, which should then be followed by the development of improved methods of controlled processing. To achieve this, new processing facilities may be needed, particularly those housing production size equipment where vacuum or controlled inert atmosphere is available.

Although not mentioned in any detail, the development of coatings and the testing of the resulting systems ranks as the number one problem to be solved and must seemingly be given high priority in any recommendations for refractory metal development.

Conclusion

In summary, we again remind you that there are difficult problems ahead. The future of many important space endeavors depends in some degree upon the extent to which the problems are solved and upon the time necessary to achieve solutions. The primary uses for the refractory metals now are generated by government requirements and the resulting markets that will be introduced will probably not be sufficient, at least initially, to stimulate widespread investment by industry in the research and development aspects of the refractory metals. Research in this area is expensive because of the high cost of

materials and equipment required. The government has and will have to continue supporting a large portion of the effort. However, there is at the present time an industry supported effort for research both for nonmilitary and military uses and it seems very likely that this effort will expand as availability of material and processing equipment increases and additional nonmilitary applications come forward to take advantage of these new materials. Expansion of research support by industry, in refractory metals, to solve mutual problems faced by both government and industry will aid greatly in overcoming the tremendous obstacles. Government and industry working together can provide the necessary effort so that the refractory metals can take their place as engineering materials.

TABLE I
COLUMBIUM ALLOYS

DESIGNATION	PRODUCER	Ti	Zr	Hf	V	Ta	Mo	W
F-48	General Electric		1	PROPRIETARY			5	15
AS-55	" "							
Cb-7	Union Carbide	7						28
Cb-16	" "	10			3			20
Cb-65	" "	7	0.8					
Cb-74	" "		5					10
D-31	Du Pont	10					10	
D-41	" "	10					8	20
82	Fansteel		0.75			32.5		
80	"		0.75					
CT2WZ	"		1			24		10
B-22	Westinghouse	1	1	5				
B-77	"		1		5			10
C-103	Wah Chang	1	0.5	10				
SCb-41	Stauffer Metals			PROPRIETARY				

THE REFRACTORY METALS

	MELTING POINT °F	DENSITY GM/CC	MODULUS psi $\times 10^6$ Cal./CM. /CM./SEC./°C	THERMAL CONDUCTIVITY	COEFF. of EXPANSION Micro./in./°F
Cb	4474	8.6	15.1	0.125	4.06
Mo	4730	10.2	47	0.34	2.7
Ta	5425	16.6	27	0.130	3.6
W	6170	19.3	50	0.397	2.55

Figure 1.

PROPULSION SYSTEM REQUIREMENT FOR REFRACTORY METALS

SOLID ROCKET

Nozzle Area

Vector Controls

LIQUID ROCKETS

Thrust Chamber

Uncooled Nozzles

NUCLEAR PROPULSION

Nuclear Ramjet

Nuclear Rocket

ION PROPULSION

Cesium Container

Ionizing Surface

AIR BREATHING RAMJET

Figure 2.

ARTISTS CONCEPTION - TYPICAL LIFTING BODY RE-ENTRY VEHICLE

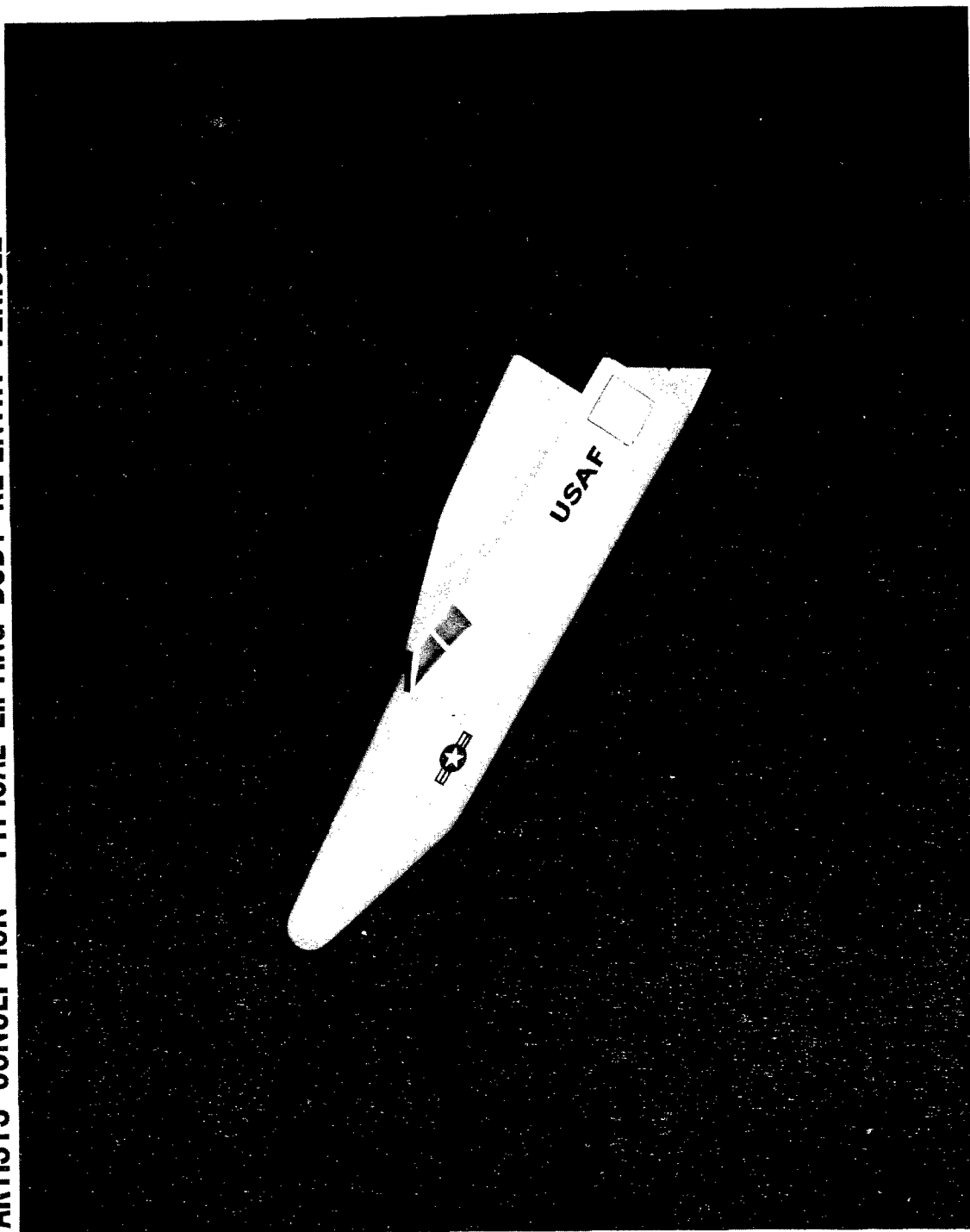


Figure 3.

ARTISTS CONCEPTION - TYPICAL GLIDER TYPE RE-ENTRY VEHICLE

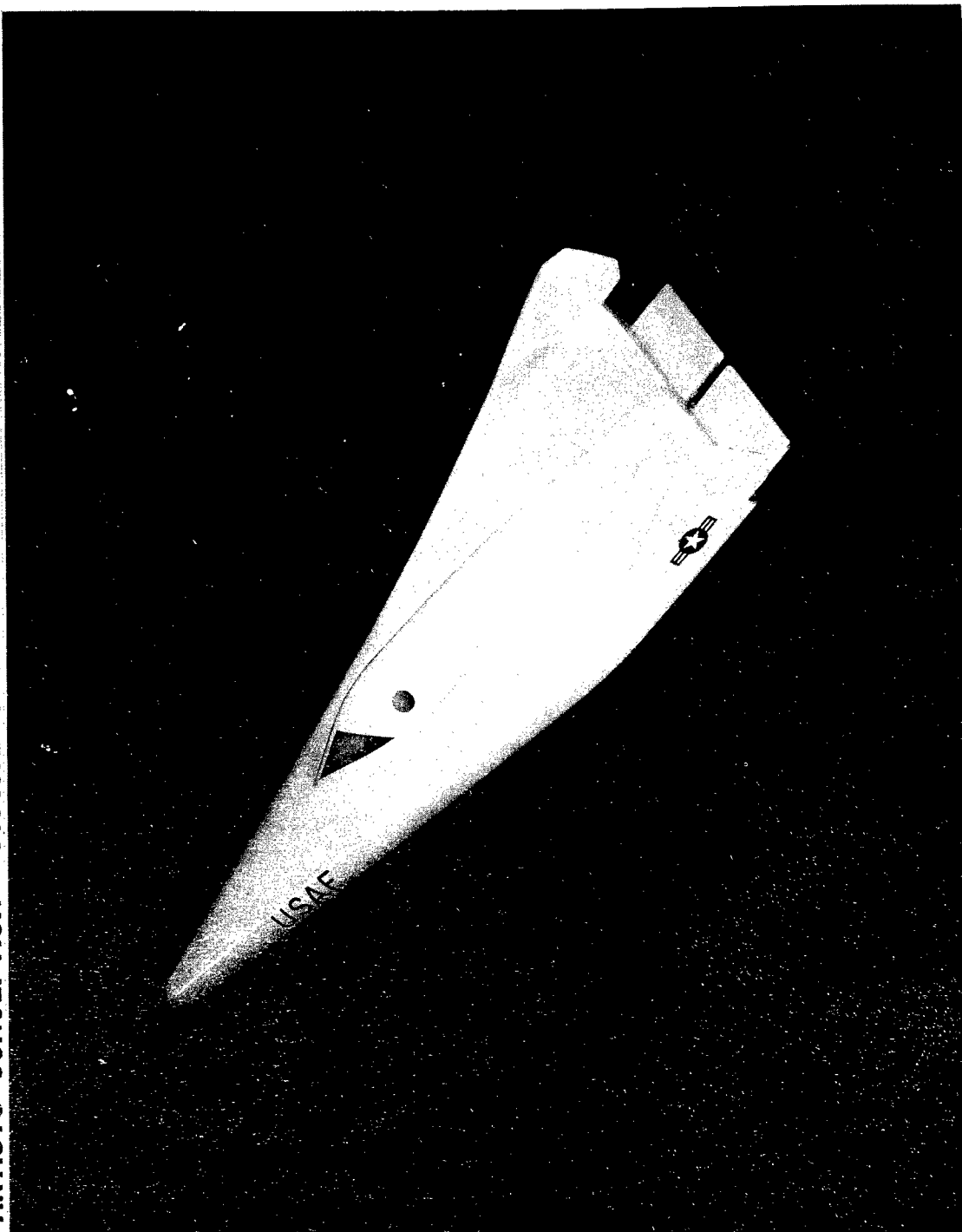


Figure 4.

EXPECTED EQUILIBRIUM TEMPERATURES DURING RE-ENTRY

	ORBITAL 26,000 Ft./Sec.	SUPER-ORBITAL 36,000 Ft./Sec.
	LIFTING BODY	
Nose	4000°F	7000-8500°F
Lower Surface	2300-2700°F	4000-4500°F
Upper Surface	2000-2500°F	3400-4000°F
	GLIDER	
Nose	3600-4000°F	6800-8300°F
Leading Edge	2700-3000°F	4500-5200°F
Lower Surface	1700-2400°F	2700-3750°F
Upper Surface	1500-2000°F	1800-3000°F

Figure 5.

SCHEMATIC OF SPACE POWER GENERATION SYSTEM

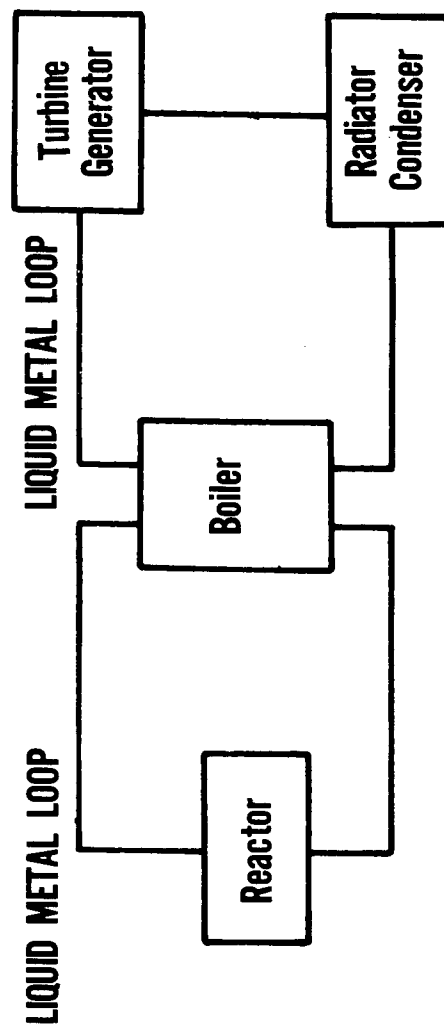


Figure 6.

TRANSITION TEMPERATURE FOR REFRACTORY METALS (RECRYSTALLIZED CONDITION)

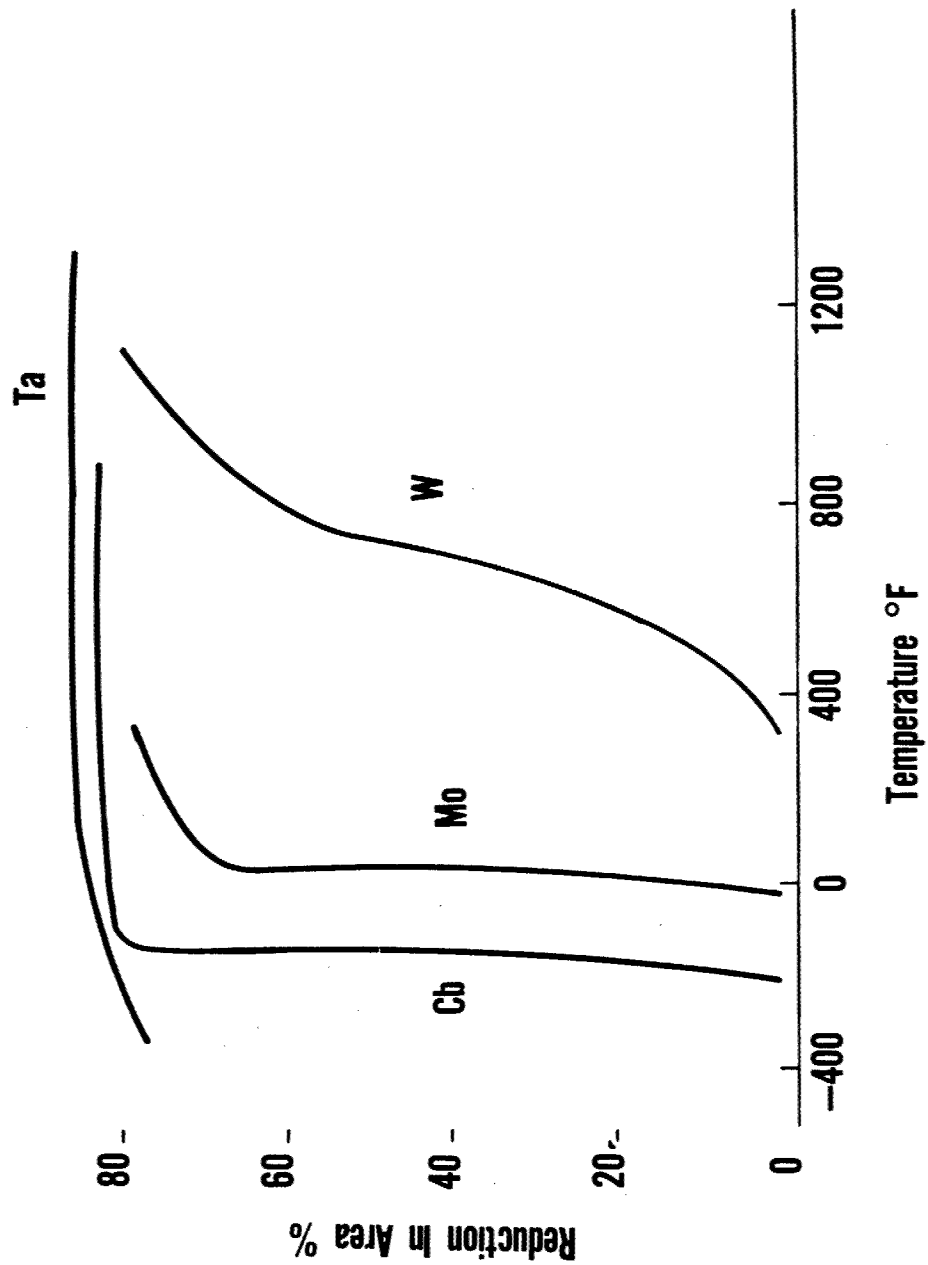


Figure 7.

EFFECT OF ALLOY ADDITION ON TRANSITION TEMPERATURE OF COLUMBIUM

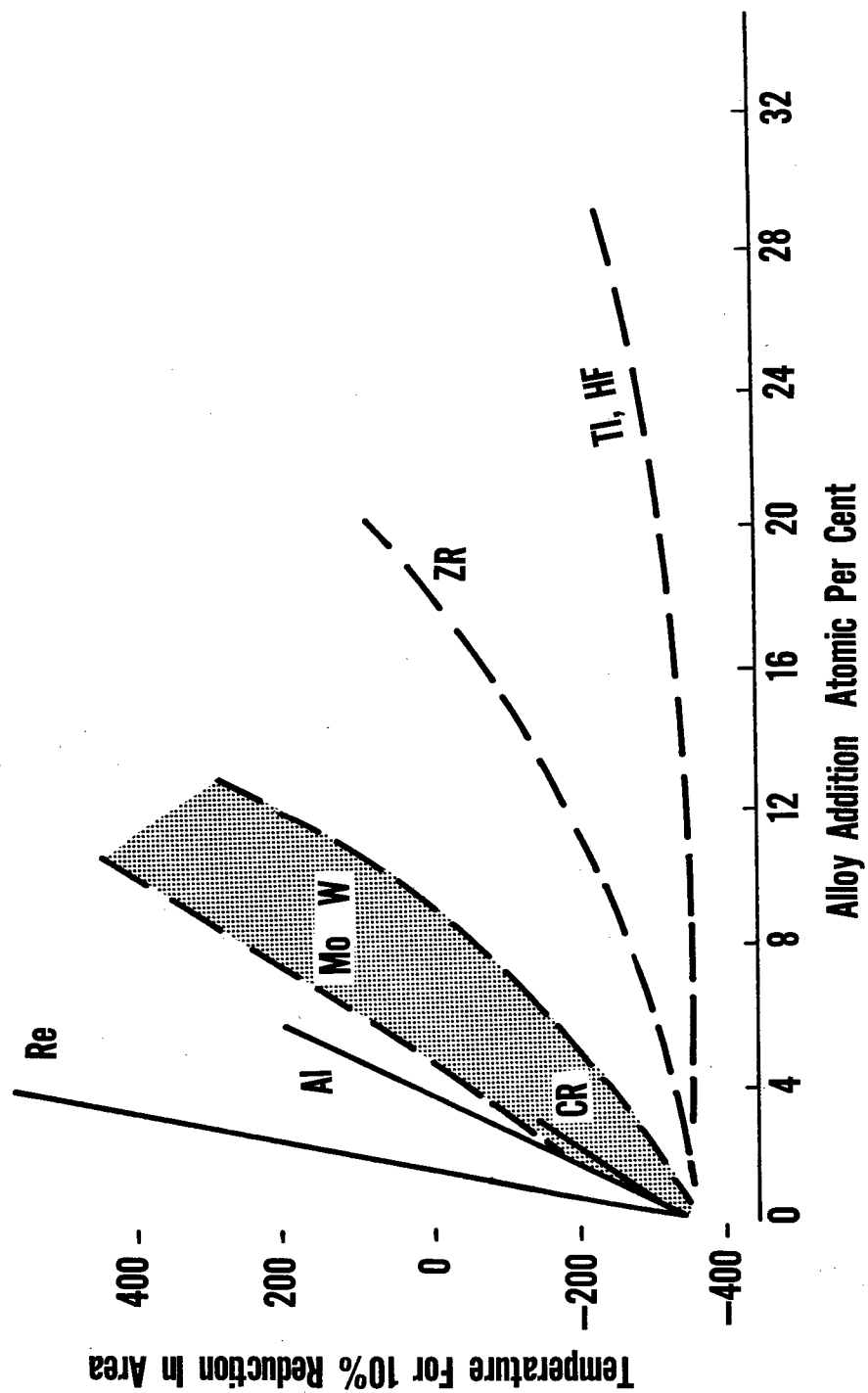


Figure 8.

MATERIALS ADVISORY BOARD

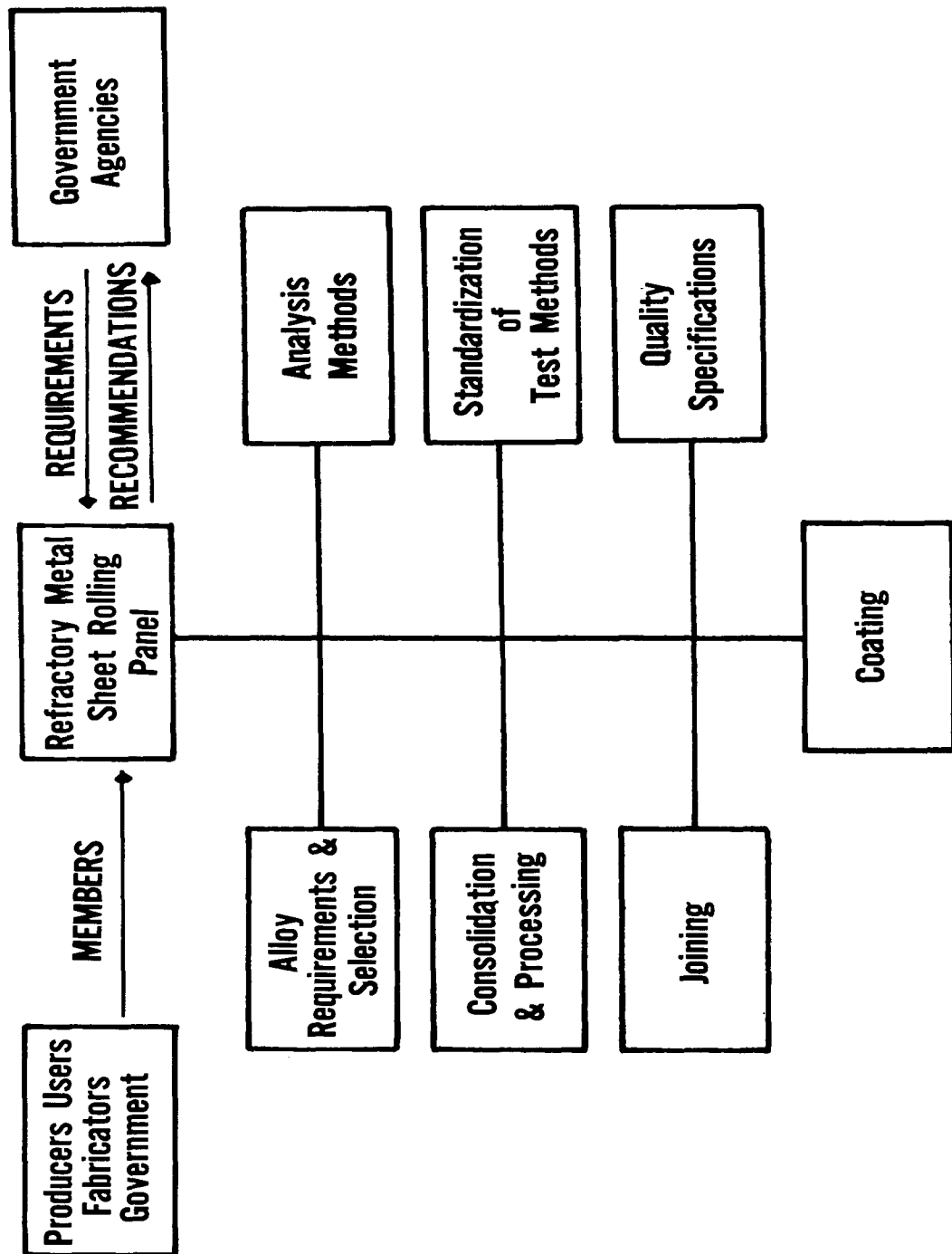


Figure 9.

ULTIMATE TENSILE STRENGTH OF COLUMBIUM ALLOYS

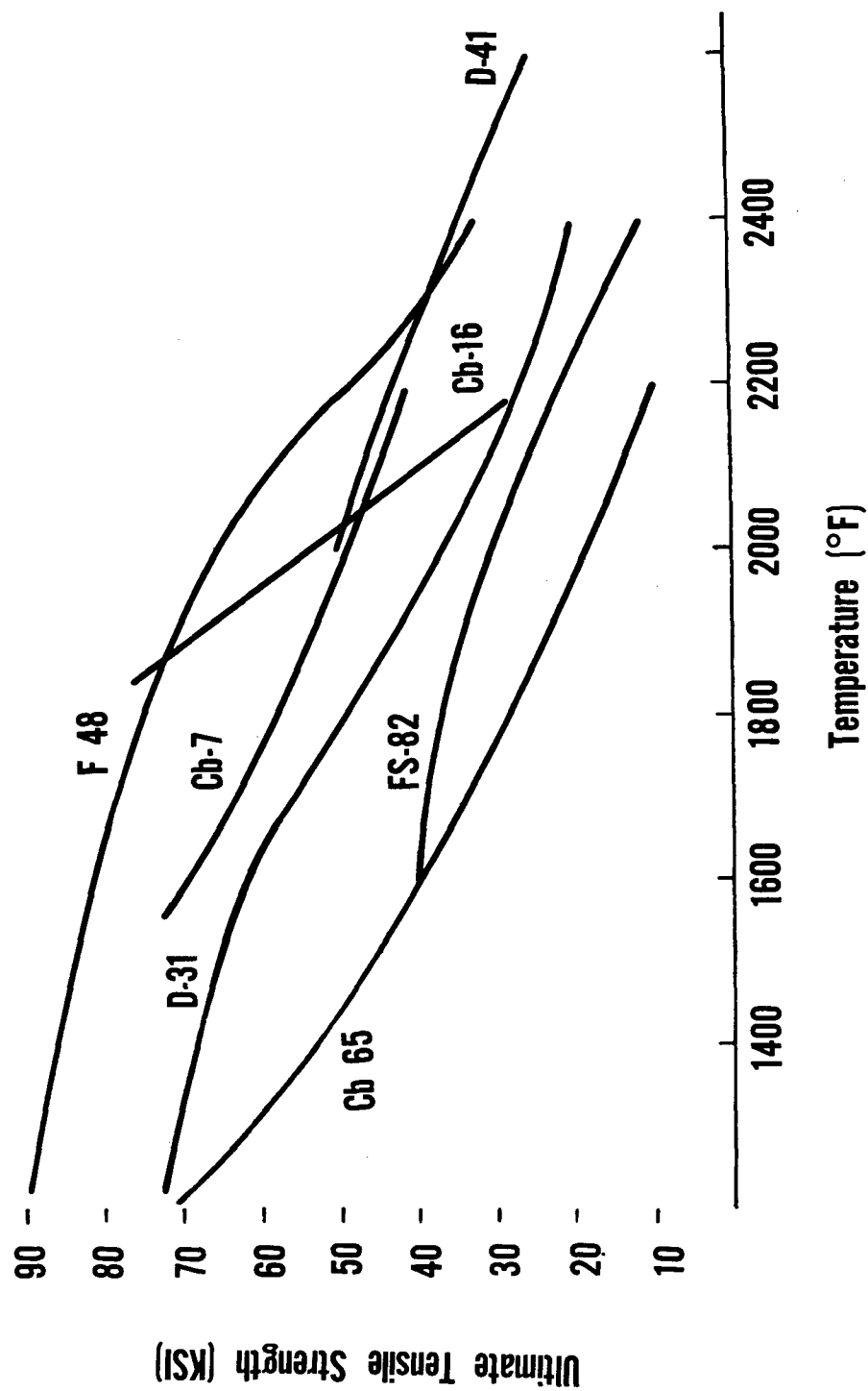


Figure 10.

ULTIMATE TENSILE STRENGTH OF COLUMBIUM ALLOYS

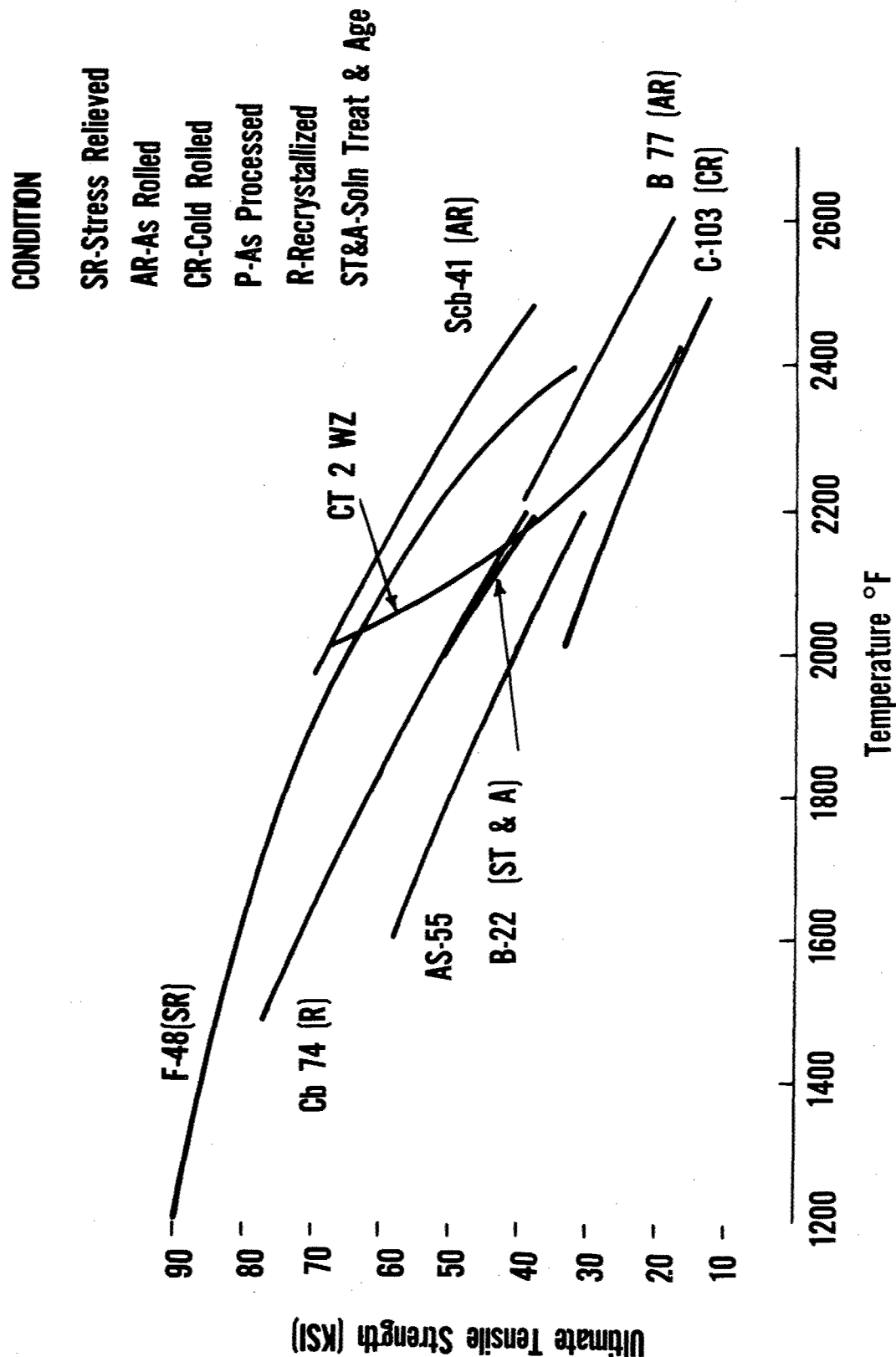


Figure 11.

ULTIMATE TENSILE STRENGTH OF TANTALUM ALLOYS

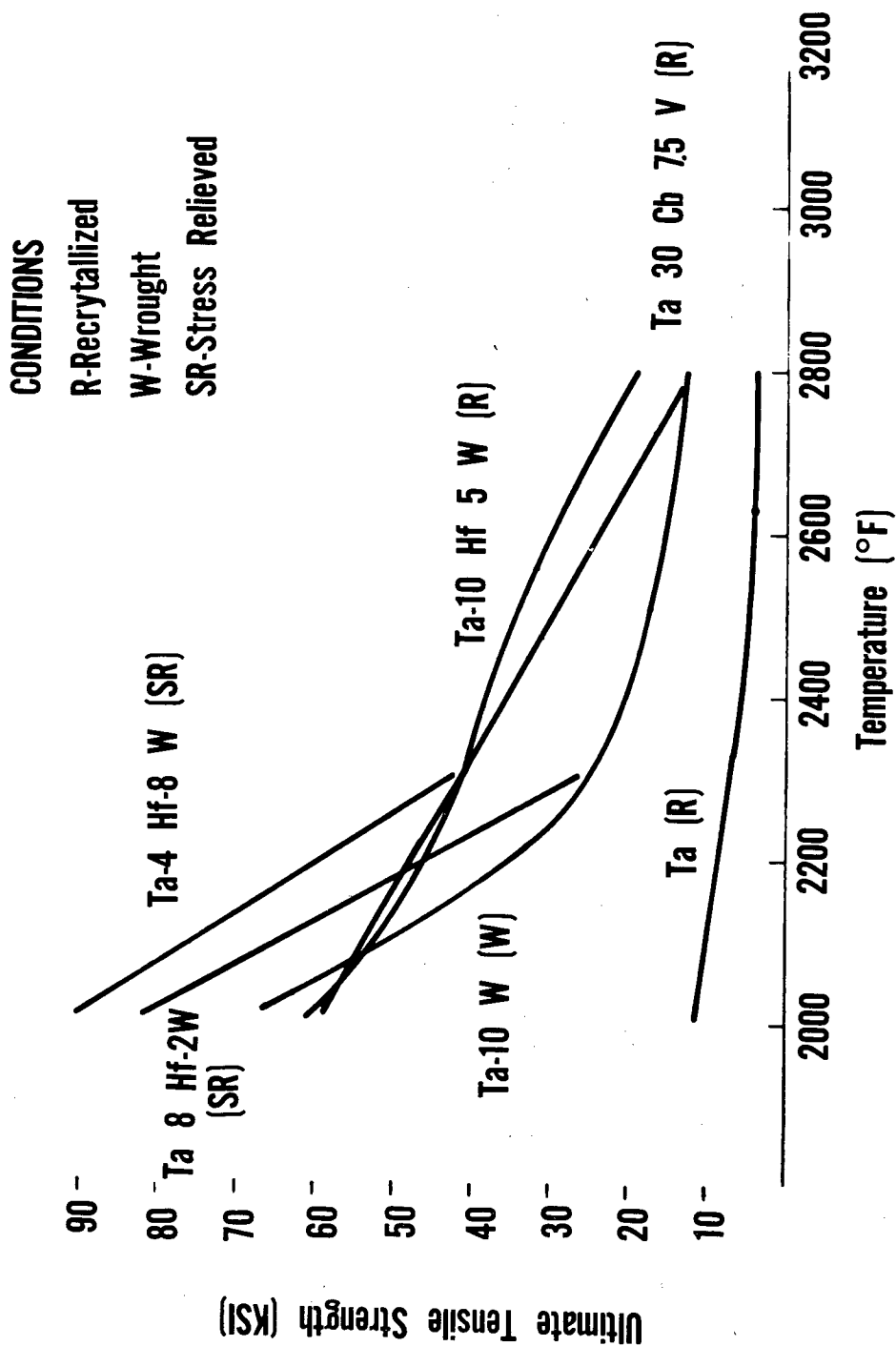


Figure 12.

ULTIMATE TENSILE STRENGTH OF MOLYBDENUM ALLOYS

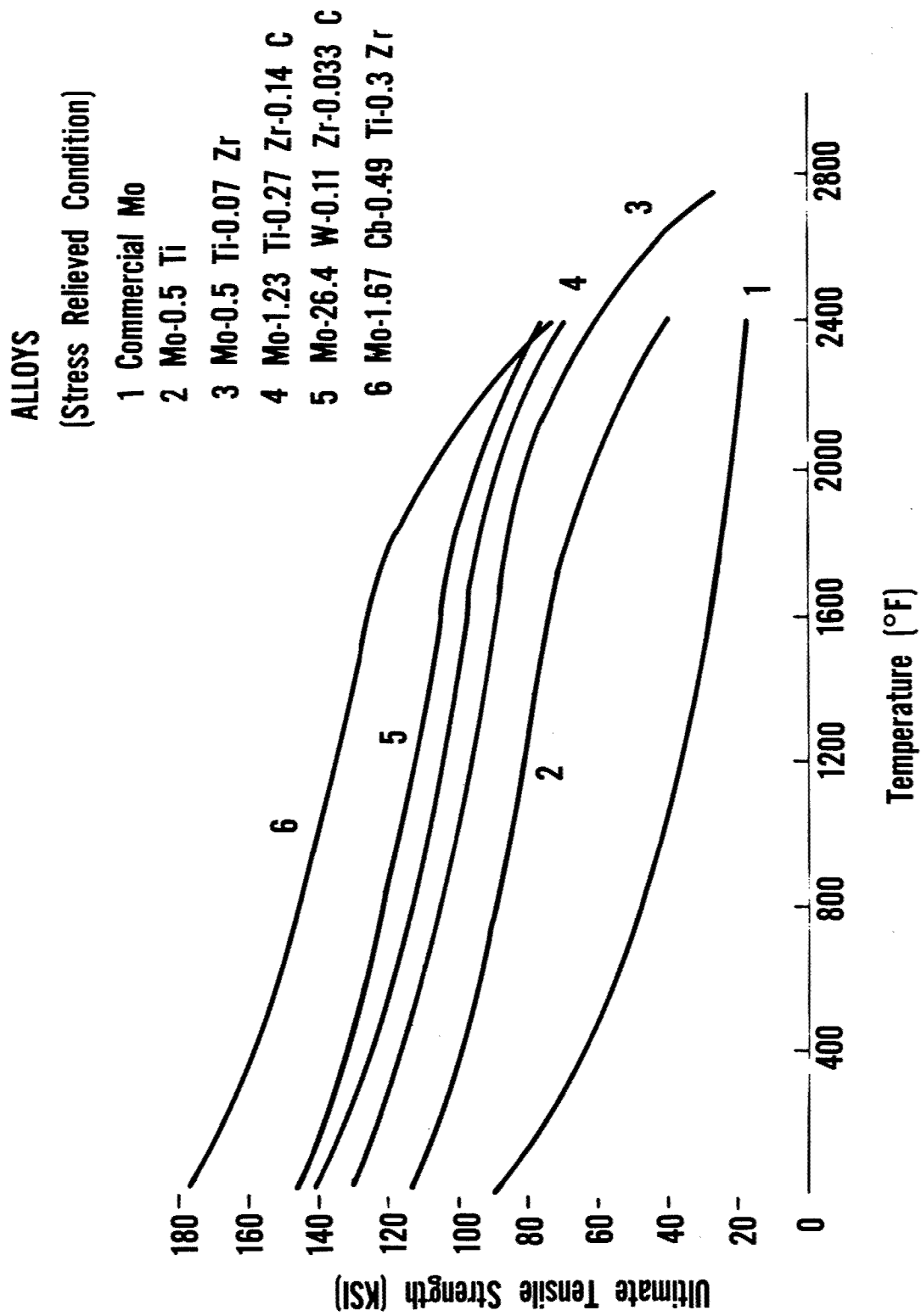


Figure 13.

ULTIMATE TENSILE STRENGTH OF TUNGSTEN ALLOYS

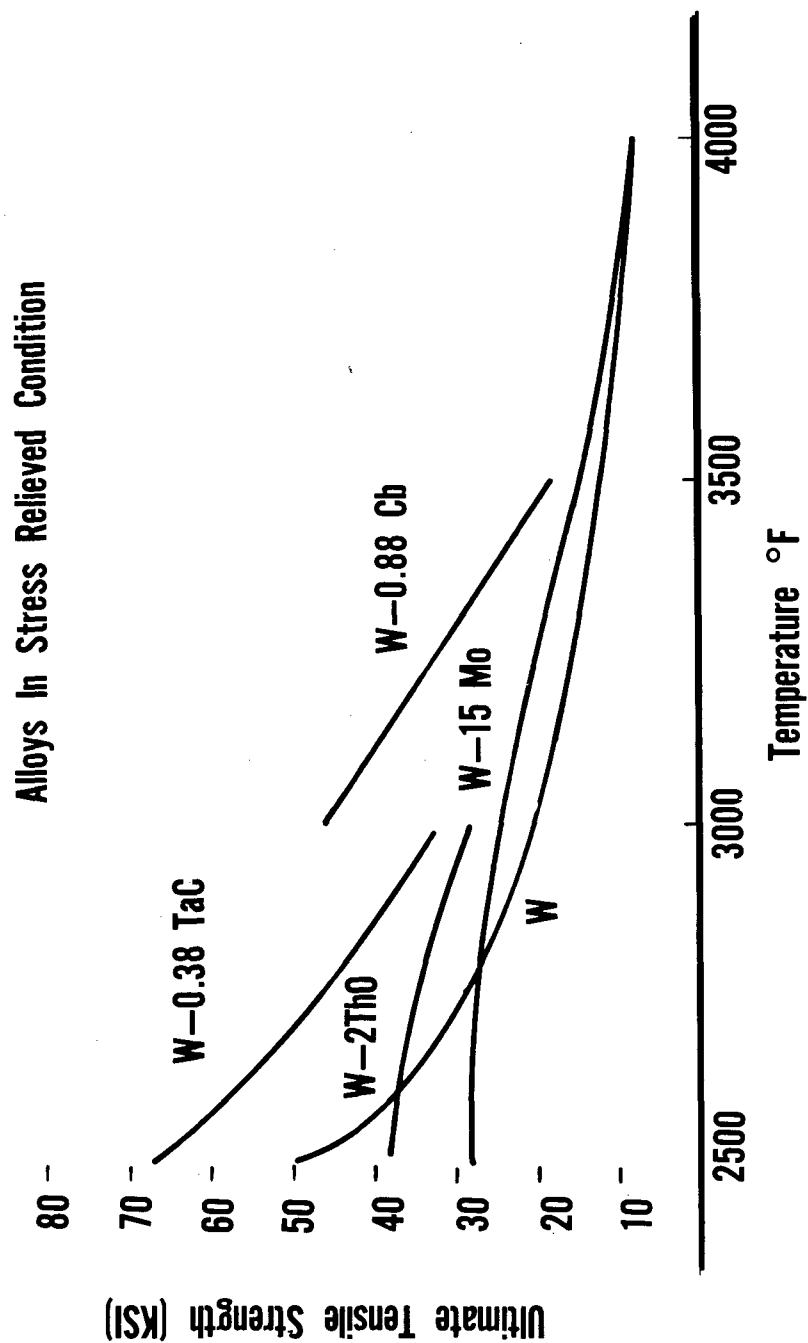


Figure 14.

ULTIMATE TENSILE STRENGTH AT 3000°F FOR TUNGSTEN ALLOYS

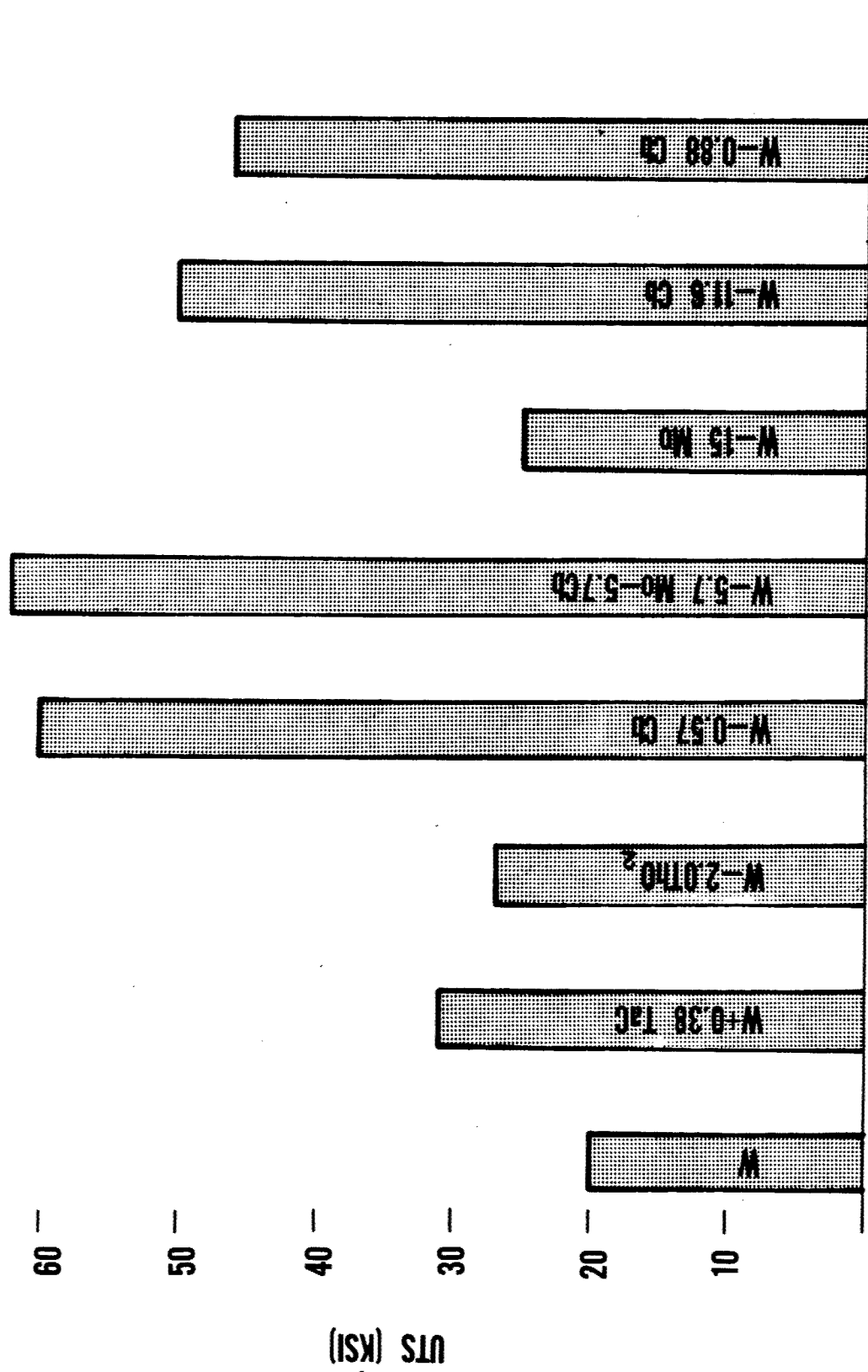


Figure 15.

FLUIDS AND LUBRICANTS

Chairman

Dr. R. L. Adamczak

Speakers

Mr. D. A. Kirk

Mr. H. W. Adams

Mr. G. A. Beane

Panel Members

Mr. R. J. Benzing

Dr. C. Tamborski

Mr. H. Schwenker

Mr. R. C. Sheard

AEROSPACE WORKING FLUIDS

David A. Kirk

Lt. John Roth

Harold Adams

Directorate of Materials and Processes, ASD

The requirements for fluids are becoming increasingly critical for the successful achievement of aerospace travel. Under intensive investigation are such materials as hydraulic fluids, flotation fluids, and heat transfer fluids. It should be pointed out that often the same class of material or fluid base stock can be utilized in more than one area. For example, organo-silicones have been put to important uses as hydraulic and heat transfer fluids. Liquid metals offer advantages for the rapid dissipation of large quantities of heat; and are also under investigation for use as hydraulic fluids under extreme conditions. Therefore, while specific fluid classes will be discussed the overall state of the art is a summation of all the effort in each area. Results from any one program area may greatly advance a second or third study.

High temperature stability is the area of greatest concern in most of the fluid programs. Organic fluids still offer promise at temperatures to 1000°F while above this region the liquid metals, liquid salts, and liquid nonmetals are undergoing intensive investigations. One of the major jobs for fluids in future applications is the removal of heat from other materials and systems so that they may function normally.

Heat Transfer and Working Fluids

Heat transfer and working fluids are of increasing importance as modern equipment, and power plants require fluids which must withstand the extreme conditions encountered in advanced aerospace applications. Working fluid temperature ranges required for some of the modern design concepts reach temperatures of 2500°F. Heat transfer fluids for modern use must cover temperatures from -80°F to +2500° and are in three general categories.

1. Organic compounds,
2. Liquid metals and
3. Liquid non-metals.

Working fluids are fluids which take heat energy and through a given working cycle convert that energy into mechanical or electrical energy. An example would be the conversion of energy in a nuclear reactor to rotary motion through a cycle or loop in which the fluid is converted into a gas which in turn energizes a turbine after releasing its energy cycled through a heat exchanger and the reactor. The simple Rankine cycle using nuclear power as the heat source would be one possible system.

Heat transfer fluids, on the other hand, have as their main function the removal of heat or control of temperature in a system. This is of particular concern in space where reliability will depend on proper temperature levels. Liquid metals are important because they can operate at the extremely high temperatures dictated by space where radiation is the only means of heat dissipation. In radiant heat transfer the T^4 function becomes the controlling parameter. Organic fluids find use in electronic systems where the actual components are temperature limited and where nonconducting properties are required.

With regard to electronic equipment design for modern aerospace systems, liquid phase coolants are the most reliable means of controlling temperature under adverse conditions. As more sophisticated vehicles are designed with space and mass conservation, increased equipment reliability of the critical electronic components demands more exacting temperature control. This can best be done by using an all liquid coolant. Temperature control of approximately one degree can be attained, which cannot be done with condensing vapor type cooling.

Figure 1 shows the operating temperature ranges of commercially available, experimental, and future desired fluids. Table 1 shows the desired physical properties for coolants and gives the properties of MLO-60-125 and MLO-60-107, two polysiloxanes which have been recently developed and are satisfactory for operation from -80° to 400°F . A large number of fluids have been examined including silanes, esters, ferrocenes, hydrogenated paraffins, ethers silphenylenes, siloxanes and silicate esters. They each possess potential for various applications.

Liquid Metals and Liquid Inorganics

Figure 2 shows some of the available liquid metals and their temperature range as working and heat transfer media. Inherent problems are introduced when liquid metals are used as fluids. They are extremely corrosive at higher temperature ranges. For example stainless steel is satisfactory at temperatures to approximately 1600°F ., but would be unsatisfactory for service to 2500°F . Physical properties of the liquid metals are not well established at the higher temperature ranges because many experimental difficulties are involved in determining them. These liquids, as could be anticipated from their position on the periodic chart, are extremely strong reducing agents. Development of the liquid metals as working fluids requires information on heat transfer coefficients, optimum operating conditions from the viewpoint of containment materials, and instrumentation compatibility. Also needed is more information on the behavior of reduced gravity fields. Table 2 gives information on some of the current research and development efforts in this field. In general, the liquid non-metals such as sulphur and aluminum bromide offer similar advantages and present difficulties similar to those of the liquid metals.

The various heat transfer working fluids offer advantages for utilization in particular applications. Present technology alone limits the upper temperature regions. As the technological changes are met, power plants and other equipment will evolve that will operate at higher and higher temperatures.

Flotation Fluids

Flotation fluids are used in inertial gyroscopes. The space which the fluid occupies is illustrated in figure 3. The inertial-gyro-wheel-carrying gimbal is precisely floated in a dense, viscous fluid. The flotation fluid reduces the torque about the gimbal rotational axis so that minute torques, corresponding to very small input angular rates, can be detected and resolved. The fluid has the dual function of providing the required buoyancy (a function of its density) and damping (a function of its viscosity). The damping function of the fluid is necessary to provide a smoothing or integrating effect on incoming rate information and to reduce the hazard of shock or vibration damage to the instrument.

General Flotation Requirements (Table 3)

1. The fluid should be radiation resistant, but otherwise exhibit similar properties to the polychlorotrifluoroethylene oil or polybromotrifluoroethylene blend.

2. After a radiation dose of 3.0×10^{10} ergs/gm C, the flotation media (2.1 cs at 160°F) may double in viscosity to 4.2 or decrease to 0.5 cs at 160°F. Density shall not change more than that which can be compensated for by 1°F change in gyro operating temperature.

3. -65°F fluidity is desired but not critical if the other requirements are met.

Two flotation fluids represent the state of the art in rate gyros using flotation fluids.

1. Polychlorotrifluoroethylene

2. Polybromotrifluoroethylene

These fluids cannot be designated as high temperature fluids. However, this is of little consequence since the temperature of the gyro is generally controlled in the range of +65° to +85°F. A wider temperature range reliability becomes important only when a gyro might not be operating as when the containing vehicle is in shipment or storage and outside temperature becomes a factor.

Many fluids have the required viscosity but few possess simultaneously high density to support the gyro wheel assembly in a reasonable floated gimbal volume. The fluids used throughout the gyroscope industry are not stable to nuclear radiation and in our present effort this is the main problem. The general requirements are shown on previous page.

A literature survey was made relative to feasible chemical structures having a high density (1.8 and above) and showing potential as radiation resistant fluids stable to a dosage of 3.0×10^{10} ergs/ gm C. Hexafluorobenzene was chosen as a starting material from which to synthesize suitable flotation fluids. The aromatic nature of the molecule indicates possibilities as a radiation resistant material and the abundance of fluorine contributes to the desired high density. The fluid must have a low vapor pressure at the gyro fill temperature so that it can be properly degassed. Calculations show that a fluid having a molecular weight of approximately 650 should satisfy this requirement. Figure 4 shows typical structures whose synthesis will be attempted.

Some gyro manufacturers appear to believe that gyros of the near future will be required to operate for long periods of time at high temperature, and under the influence of high nuclear fluxes. Typical conditions expected are shown in table 4.

The manufacturers appear to believe that rate gyros can be designed and constructed to operate without liquid bearing lubricants and entirely without a flotation fluid media. The gimbal assembly might be electrically floated and dampened by a magnetic field. This type gyro would eliminate the use of flotation fluids, resulting in a weight reduction, fluid-component compatibility, and fluid gassing.

Hydraulic Fluids

The state of the art in hydraulic fluids is shown in table 5. Hydraulic fluids qualified under MIL-H-5606A are in general use throughout the Air Force, Navy and Army. MIL-H-5606B, is a tentative specification covering a super clean fluid with a better shear stable viscosity improver than that used in MIL-H-5606A. It is hoped that fluids qualified under this specification (MIL-H-5606B) will service both aircraft and missiles. MIL-H-5606A fluids are petroleum based and generally contain TCP (anti-wear additive), acryloid (viscosity index improver), and phenothiazine or PANA (antioxidant). The only fluids qualified under MIL-H-8446B are disiloxane based, with appropriate additives. Approximately 14 percent diester fluid is added to the disiloxane to produce the necessary neoprene rubber swell characteristics.

Research and Development Effort

The major research and development effort is for a type 4 system hydraulic fluid. It is anticipated that this fluid will be under specification by 1 July 1961; it is petroleum based and is usable as a hydraulic fluid up to +550°F. It is a super-refined, deep dewaxed, paraffinic mineral oil and has been designated MLO 60-294. The research effort responsible for the development of this fluid was carried out by the Petroleum Refining Laboratory, Pennsylvania State University, under contract with the Air Force. Figure 5 illustrates the general refining schematic for the origin of the base stock.

The main problem was to remove, by hydrogenation, all polar impurities, double bonds and open terminal bonds without excessive hydrocracking.

Although fractions 1 and 2, as described, exhibited excellent thermal stability at the expected operating temperatures, the low temperature properties were a problem. Low temperature dewaxing studies were carried out to improve the low temperature fluidity. The Laboratory method, using a mixture of methylethyl ketone and methylisobutyl ketone as the solvent proved to be very efficient at -65°F to -80°F. This treatment yielded 85 percent oil (-75°F pour point) and 15 percent wax (+40°F pour point). The deep or low temperature dewaxing was followed by vacuum stripping to remove the dewaxing solvent and any hydrocracked materials from the refining steps. This was followed by acid treatment to remove trace impurities and unsaturation caused by steps following hydrogenation.

Tables 6, 7 & 8 show data obtained on the formulated dewaxed oil (MLO 60-294).

The data in table 8 shows that excellent wear properties can be expected from this high temperature mineral oil. This is a very important property relative to hydraulic pump life and reliability.

A synthesis and evaluation program is being carried out on fire resistant hydraulic fluids for use over the temperature range of -65°F to 450°F and +40°F to 800°F. The program initially concentrated upon a means of molecular evaluation which could classify specific chemical bond types, relative to their fire resistance. The general type classes involved were: halocarbons, phosphine oxides, aromatic and heterocyclic compounds. Using flame velocity coefficient measurements, it was intended to correlate chemical structure with flammability. The following questions were to be answered during these initial studies:

1. What are the fire retardant atoms and groups and what are their efficiencies?
2. Are there any synergistic effects shown by two or more fire retardant atoms or groups?
3. What are the optimum linkages for incorporating a fire retardant atom or group in a molecule?
4. What are the major synthetic problems to be anticipated in the design of a fire resistant fluid?

The general observation (April 1961) appeared to be that the Phosphine oxides held promise as yielding a fire resistant -65°F to 450°F hydraulic fluid and the heterocyclic class, such as derivatives of pyridine, to yield a +40° to 800°F fluid.

Table 9 illustrates autogenous ignition temperature comparisons of halides with their hydrocarbon analogs. This table shows that the position and halogen type as well as halogen combinations have a marked influence on the AIT also, the ratio of halogen to carbon-hydrogen.

It is felt that mineral oils can be reliably used as hydraulic fluids up to 700°F. Above 700°F, the polyphenyl ether fluids may become useful but will probably not be usable over 850°F for any appreciable time. For hydraulic systems requiring fluids 1000°F or higher, it appears that considerable promise lies in the inorganic fluids. Phosphorus-nitrogen polymers have been made by DuPont, under contract to the Air Force, which have liquid ranges from 0°F to 1000°F and higher. Considerable effort is needed to derive suitable prototype fluids. However, within the next year, some inorganic fluids, with thermal stability in the 1000°F range should be available. Figure 6 shows a typical structure as of April 1961. Other possible approaches are in the area of liquid metals and salts.

General Electric Company under contract with the Air Force has been studying this area for several years. Current emphasis is in feasibility of system operation and design of servo valves for use in liquid metal systems.

In summary it should be pointed out that fluid synthesis in the case of nonmetallic materials and property studies in the case of liquid metals and salts are the areas requiring research and development for all fluid classes. Initially, high temperature stability and operation will be required prior to study of other characteristics such as radiation tolerance.

REFERENCES

1. Barsness, D.A., WADD Technical Report 60-795 Part 1 (December 1960).
2. Weatherford, W.D. Jr., Tyler, J.C. and Ku, P.M., WADC Technical Report 59-598 (December 1959).
3. NASA-AEC Liquid-Metals Corrosion Meeting, NASA TN 0-769 February 1961.

TABLE 1
SILICONE FLUIDS

PHYSICAL AND CHEMICAL PROPERTIES	UNITS	DESIRED PROPERTIES	MLO-60-125	MLO-60-107
CHEMICAL COMPOSITION		N / A	METHYL POLYSILOXANE	METHYL POLYSILOXANE
COLOR		N / A	CLEAR	CLEAR
POUR POINT	°F	< -80	BELOW -134	BELOW -90
FLASH POINT	°F	> 400	480	515
FIRE POINT	°F	> 400	600	640
SURFACE TENSION	dynes/cm	> 30	21.7	23.
VISCOSITY AT 400°F	CENTISTOKES	1	2.	2.2
210°F			6	6.3
100°F			13	16.
-65°F			164	232.
-80°F		100-300	251	371
VAPOR PRESSURE AT 600°F mm Hg			35	46
500°F			8	22
400°F		<100	2.4	12.5
300°F			.6	6.2
200°F			.1	2.4
100°F			.1	1.3
DENSITY-TEMP.	gm/cc			
400°F			0.797	0.810
210°F			0.885	0.892
100°F			0.939	0.946
77°F			0.950	0.960
40°F			0.970	0.979
0°F			0.985	0.998

TABLE 2
SUMMARY OF SELECTED CURRENT HIGH TEMPERATURE LIQUID METAL PROGRAMS (3)

LIQUID METAL	TYPE OF PROGRAM	CONTAINMENT METAL	MAX. TEMP.	STATUS
Rb	BOILING CONDENSING LOOP	316S.S	1900°F	ALMOST READY FOR OPERATION
Rb	BOILING CONDENSING LOOP	SAME AS ABOVE, EXCEPT MATERIAL IS Nb-1Zr		LOOP NOT BUILT YET
Na	TWO PHASE LOOP	304 S.S.	1832 °F	————
NaK	PUMPING LOOP, CORROSION	316 S S.	1500°F	TERMINATED
Na	REFLUX CAPSULES	Nb-1 Zr	2200-2300°F	PLANNED
Na	BOILING PUMPED LOOP	— —	2400°F	DESIGN STAGE
Na ₁ K	TWO BOILING & CONDENSING HEAT TRANSFER LOOPS	HS-25, Nb-1Zr	2200°F	PRELIMINARY EVALUATIONS
Na ₁ K	TWO PHASE THERMAL CONVECTION LOOPS	INCONEL, Nb-1Zr	2500°F	INCONEL LOOPS RUNNING
Li	HEAT TRANSFER Li TO Ta	— —	2400°F	IN PROGRESS

Note: for explanation of table 3 (see page 340)

Table 4

FUTURE TYPICAL CONDITIONS FOR FLOTATION

OPERATING TEMPERATURE RANGE	-65° To 700°F
Time (Hrs.)	25,000
Nuclear Flux	1.0×10^{12} To 10^{15} Ergs/gm/C

Table 5

HYDRAULIC FLUID STATE-OF-THE-ART

BASE CHEMICAL TYPE	SPECIFICATION NO.	TEMPERATURE RANGE
Petroleum	MIL-H-5606B	-65°F To 275°F
Synthetic	MIL-H-8446A	-65°F To 400°F
Petroleum	Proposed MIL-H-27601 USAF	-40°F To 550°F
Petroleum Or Synthetic	MIL-H-(?)	0°F To 700°F
Synthetic (Inorganic)	MIL-H-(?)	0°F To 1000°F

Table 6

SUPER REFINED, DEEP DEWAXED, PARAFFINIC MINERAL OIL

Viscosity (Centistokes)	At	-65°F	22,859
		-40°F	2,820
		0°F	306
		100°F	14.08
		210°F	3.18
		400°F	1.12
		550°F	0.74
ASTM Slope (210°F To 100 °F)			0.784
Pour Point, °F			-80
Flash Point, °F			385
Fire Point, °F			430
Initial Decomposition Point, °F (Isoteniscope Method)			678

Table 7

PHYSICAL PROPERTIES (DENSITY, $d_4^{20} = 0.840$)

	0°F	200°F	400°F	500°F
Coefficient Of Expansion cc/cc/°F x 10 ⁴	4.4	5.4	6.4	
Thermal Conductivity BTU/ft ² /hr/ °F/ft	0.0813	0.0749	0.0700	0.0676
Specific Heat (BTU/lb/°F)	0.440	0.537	0.635	0.684
Bulk Modulus, psi x 10 ⁻⁵ Av. Value For 0 To 10,000psi	3.2	2.2	1.2	0.7
Vapor Pressure (mmHg)		2.0	21.0	84.0
Density ; (gm/ml)	0.866	0.796	0.726	0.691

TABLE 8

WEAR DATA

Shell 4-Ball Wear at 75°C, 1200rpm, 2hours	Load (Kg)	Scar (mm, diam)
	40	0.21
	10	0.26
	40	0.53
at 400°C, 600rpm, 2hours	4	0.19
	10	0.25
	40	0.48

TABLE 9

STRUCTURE	AIT, °F (Halide)	AIT, °F (Hydrocarbon)	AIT (Halide) — AIT (Hydrocarbon)
$F(CH_2)_4$	525	761	- 236
$Br(CH_2)_4Br$	765	761	+ 4
$Cl(CH_2)_2Cl$	825	959	- 134
$Br(CH_2)_2Br$	960	959	+ 1
$Cl(CH_2)_4Cl$	445	761	- 316
$Cl(CH_2)_2Cl$	825	959	- 134
$CH_3(CH_2)_2Cl$	790	871	- 81
$CH_3(CH_2)_2Br$	1000	871	+ 129
$CH_3(CH_2)_3Br$	500	761	- 261
$CH_3(CH_2)_2Br$	1000	871	+ 129

TABLE 10

BASE CHEMICAL TYPE	SPECIFICATION NO.	TEMPERATURE RANGE
PETROLEUM	MIL-H-5606B	-65°F TO 275°F
SYNTHETIC	MIL-H-8446A	-65°F TO 400°F
PETROLEUM	PROPOSED MIL-H-27601USAF	-40°F TO 550°F
PETROLEUM OR SYNTHETIC	MIL-H-(?)	0°F TO 700°F
SYNTHETIC (INORGANIC)	MIL-H-(?)	0°F TO 1000°F

LIQUID COOLANTS OPERATING TEMPERATURE RANGE

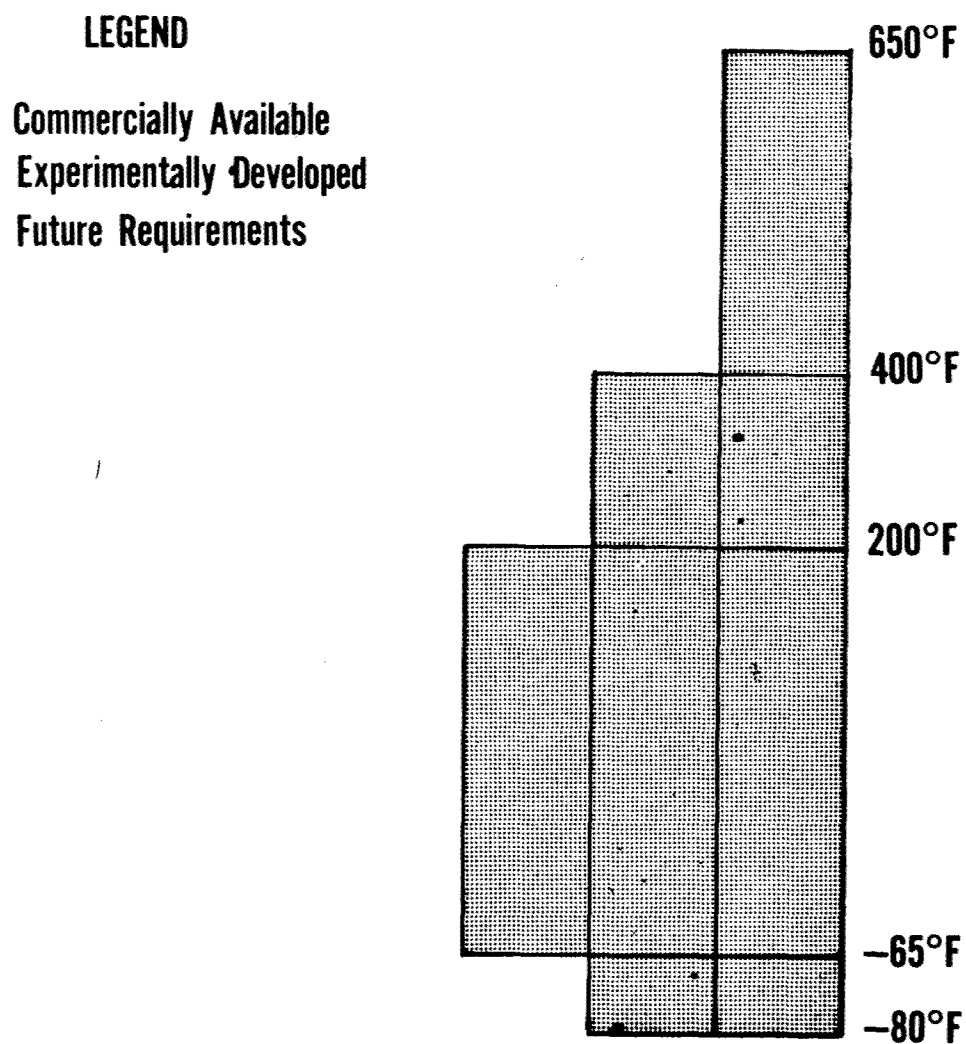


Figure 1.

LIQUID METAL WORKING FLUIDS °F

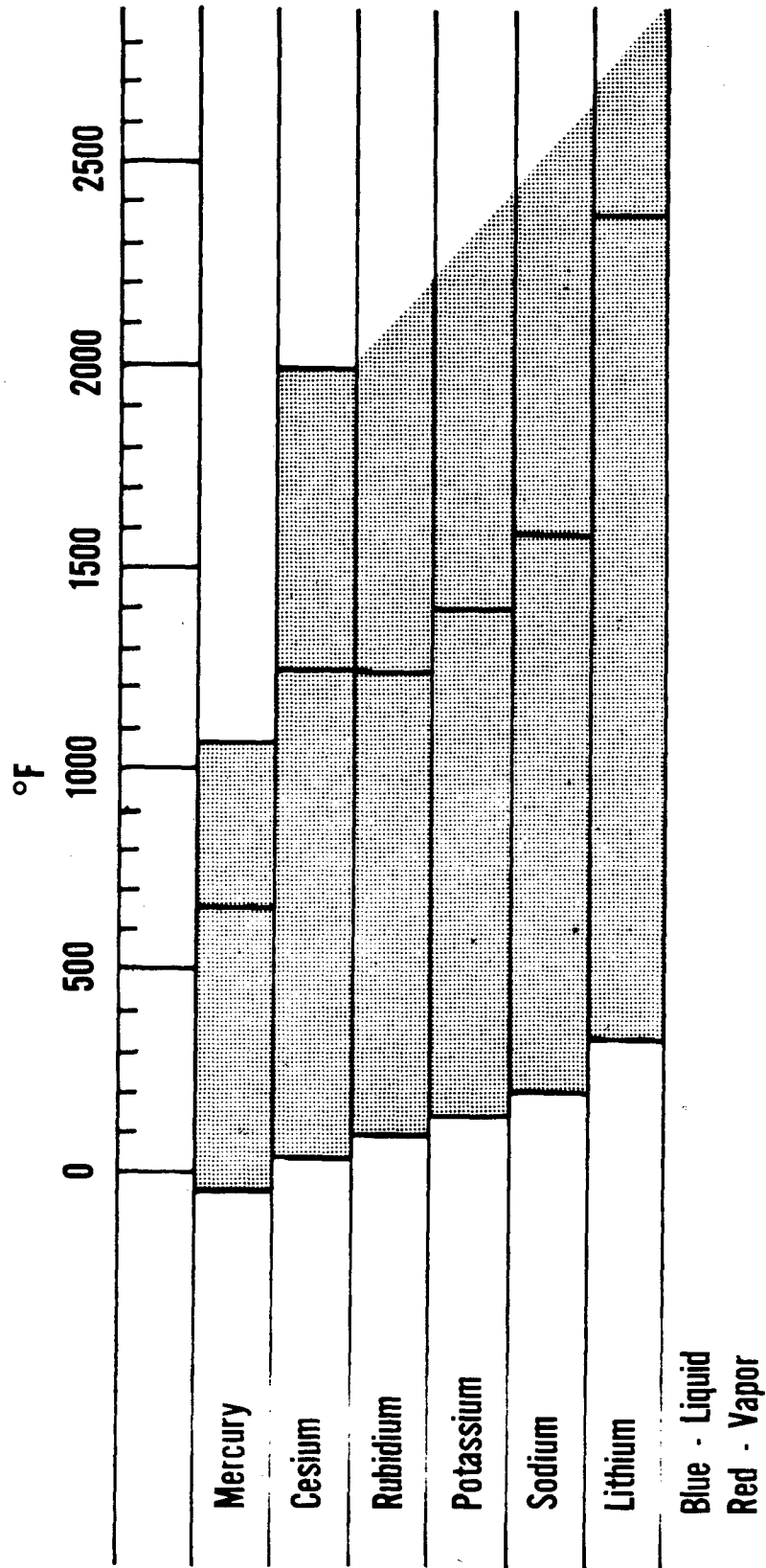


Figure 2.

DIAGRAM OF FLOTATION FLUID AREA

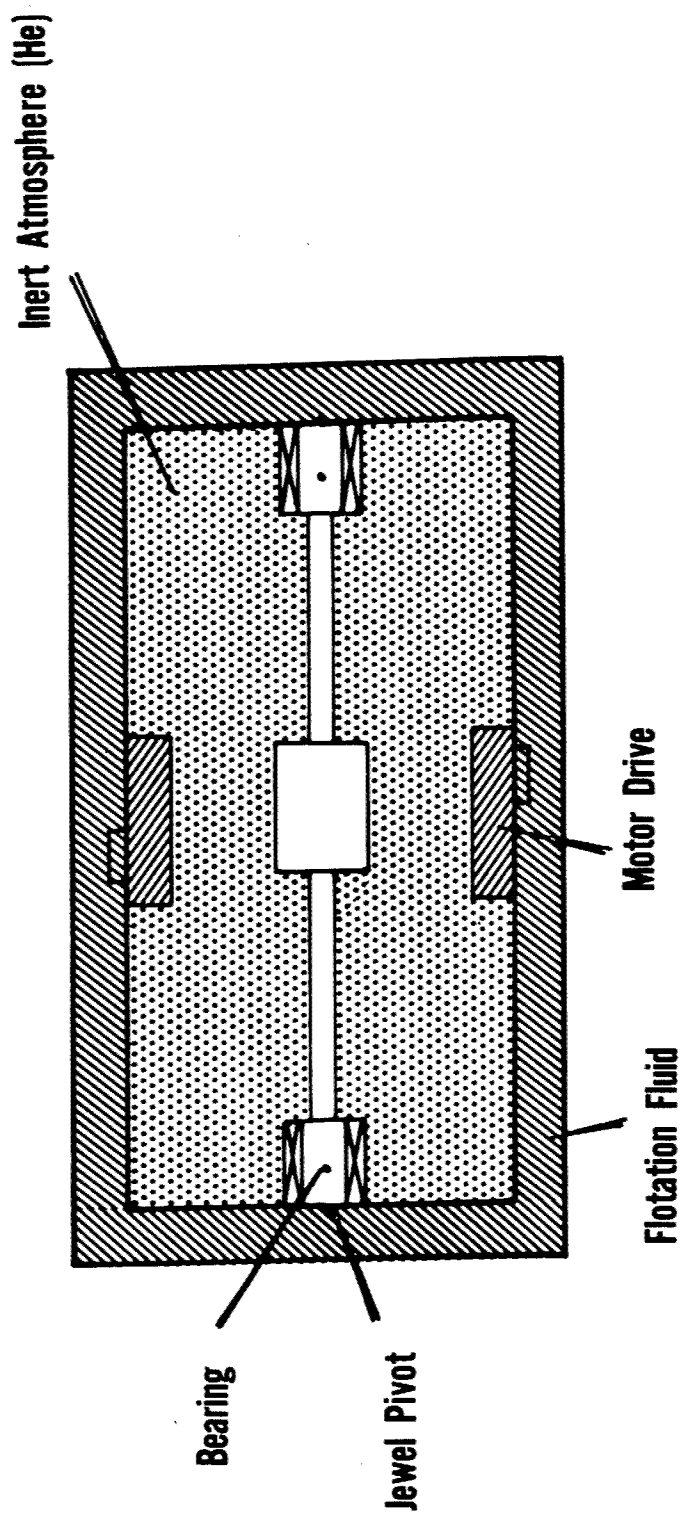


Figure 3.

POSSIBLE SUITABLE STRUCTURES

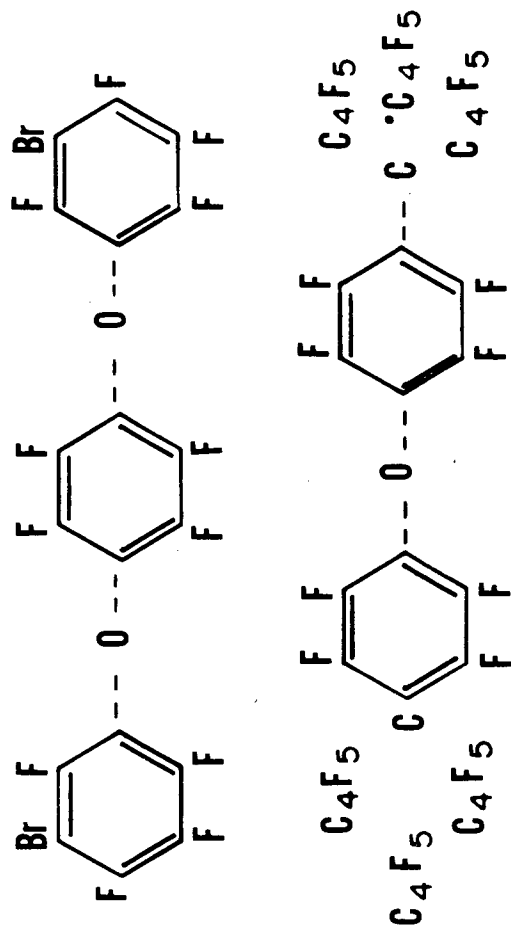


Figure 4.

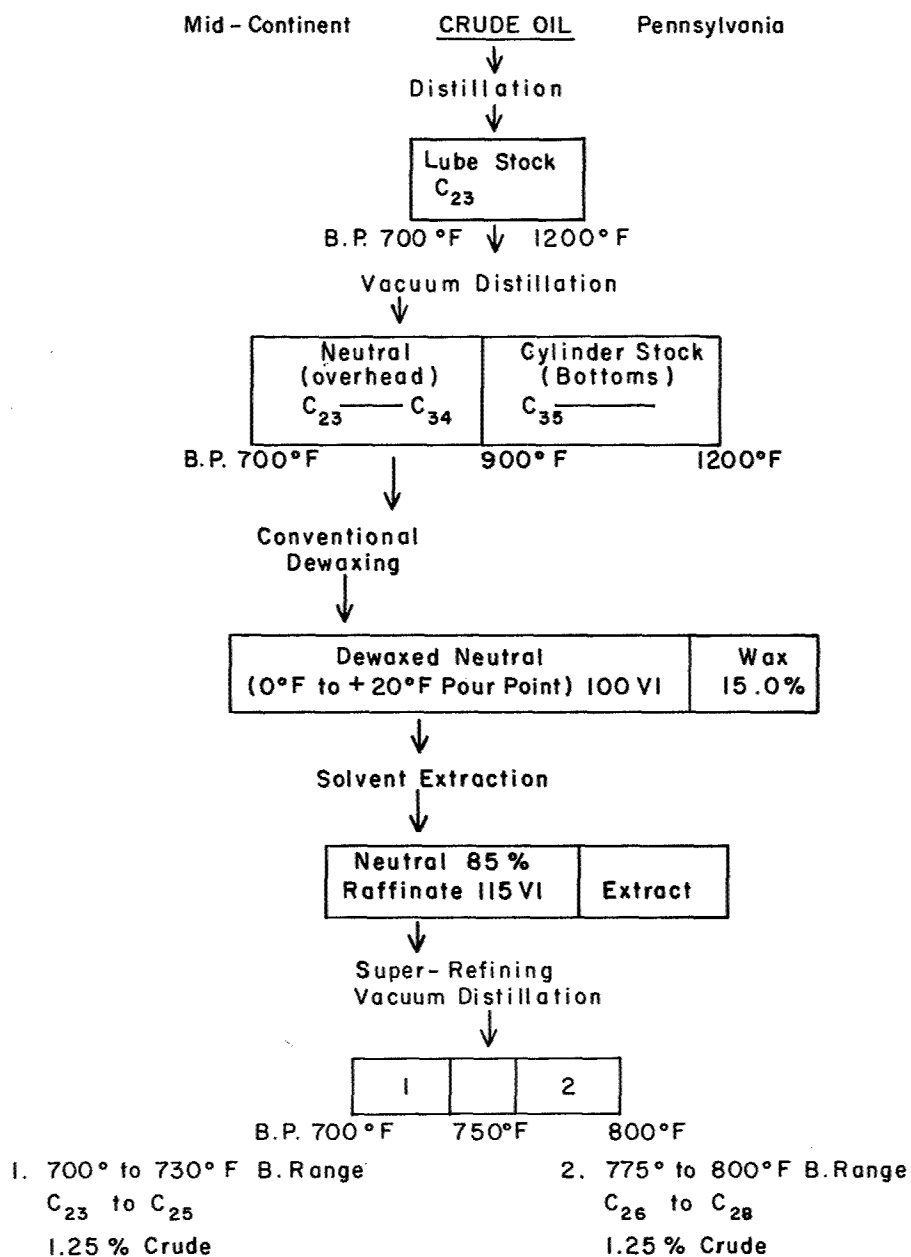
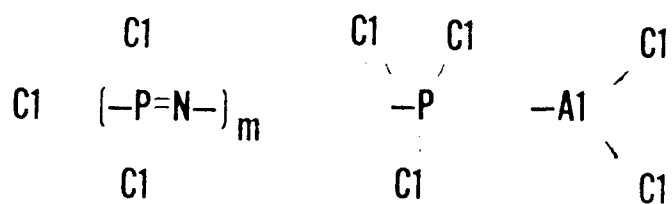


Figure 5.

TYPICAL INORGANIC FLUID



Lewis Acid Stabilized Phosphonitrilic Chlorides

Does Not Polymerize Up To 550°C

Hydrolytically Unstable

Figure 6.

AEROSPACE LUBRICANTS

Harold W. Adams

Directorate of Materials and Processes, ASD

The purpose of this paper is to review the past and current technological status and future plans for liquid lubricants, greases, and solid films. This endeavor is specifically concerned with the efficient and reliable lubrication of power systems, control systems, and their associated subsystem components. Research and development effort, devoted to the advancement of the state of the art, may well deal with techniques and methods of accomplishing efficient lubrication as well as strictly material investigations. The answer to certain lubrication problems may lie in the knowledge of conditions and change thereof, rather than the necessity of using a new lubricant material.

Liquid Lubricants

Turbojet Lubes - Work has been in progress, for the past several years, to derive a satisfactory turbojet lubricant for use in the 500°F bulk oil temperature range. It is necessary to place emphasis upon the oxidation stability of the base fluids when considering their severe operational environments. Figure 1 illustrates the state of the art in turbojet lubricants relative to military specifications.

It is virtually impossible to synthesize a base fluid possessing all the performance capability required in the lubrication of a turbojet engine. Severe oxidizing conditions and high mechanical loads dictate the use of chemical additives to improve the performance characteristics of the base fluids. Research and development programs on both base fluids and additives are carried out concurrently. Two specific approaches are being followed for the derivation of high temperature turbojet base fluid lubricants. Figure 2 shows the general chemical structures concerned with the first of these approaches, "pyrazine" derivatives. Figure 2 shows the basic pyrazine nucleus which can be tetra substituted, if necessary. As shown, three different chemical bond types were investigated relative to thermal stability. Of the three types, the anilino substituted proved to be the most thermally stable. The anilino pyrazines showed good thermal stabilities at 600°F, good oxidation stability at 500°F and good viscometric properties. Most all the property data obtained on these three type pyrazine derivatives indicate the anilino or amino substituted pyrazines were thermally unstable. Cleavage generally occurred between the R group and the sulfur atom at relatively low temperatures, such as 450° to 500°F. The phenoxy substituted pyrazines showed good thermal and oxidation stability at 500°F. However, at 600°F, the phenyl group appeared to migrate to the 1 position nitrogen. Because of this thermal rearrangement at 600°F, the phenoxy pyrazines do not show exceptional promise. The rearrangement appears to be of a free radical nature; therefore, chemical blocking the other phenyl positions would not aid the situation.

Figure 3 shows two pyrazine isomers, a 2,3 and a 2,6 substituted pyrazine. The 2,6 substituted has slightly better low temperature properties than the 2,3 substituted. The 2,6 isomer has a pour point of approximately -40°F. These isomers both possess good oxidation stability at 500°F, better than the MIL-L-9236B fluids. Additional substitution is planned for the 2,6 substituted fluid to increase the molecular weight. This may be accomplished in several ways and silyl substitution at the 2 or 5 positions will be tried.

Figure 4 shows a 2-anilino, 3-silyl pyrazine which has the best liquid range properties of any prototype fluid prepared to date. This fluid has a pour point of approximately -90°F . However, in high temperature tests, infrared spectra showed the presence of an olefin. This was attributed to cleavage between the carbon and pyrazine ring at the 3-position, forming a vinyl silane. Means have now been devised to methylene link the silyl group to the pyrazine ring. This will eliminate the possibility of olefin formation.

Another practical approach to suitable liquid range pyrazine fluids for 500°F turbojet lubricants are all alkyl substituted pyrazines or possibly halo-alkyl pyrazines (Halo = fluorine). A 2-nonyl, 5-heptyl pyrazine fluid was made and showed surprising oxidation stability at 500°F relative to other pyrazine fluids. It appears possible to synthesize a higher molecular weight all-alkyl pyrazine fluid which will be suitable as a high temperature lubricant for oxidizing environments. Comparative data on an alkyl pyrazine versus other fluids is shown in figure 5. In summary on pyrazine fluids, much work is needed and unlimited possibilities (as to chemical structures) exist to synthesize suitable high temperature fluids.

The second approach to base fluids for high temperature turbojet lubricants is narrower in scope but appears quite promising. This approach involves the synthesis and evaluation of aromatic ester fluids. Figure 6 shows a prototype aromatic ester, (Resorcinol di-neoheptanoate) representative of the type materials being investigated. It appears to possess the necessary properties for a high temperature turbojet lubricant. This fluid was made from 1,3-resorcinol esterified with neoheptanoic acid. This fluid has a pour point of approximately -50°F . The oxidation stability appears comparable to the polyphenyl ethers but is more volatile. At any rate, the aromatic esters show considerable promise and higher molecular weight fluids will be synthesized to reduce volatility.

Other promising approaches will undoubtedly evolve from current basic research programs on fluid synthesis. For example, figure 7 shows a new fluid material which has some interesting properties. This fluid is less attractive than the polyphenyl ethers relative to fluid range, thermal and oxidation stability.

Still other possibilities lie in the areas of perfluoroalkyl and perfluoroaryl-aromatic compounds. No structures are shown here since the synthesis of these is in the fetal stages. However, as oxidizing environments become more intense, the perfluorinated compounds become more attractive.

Instrument Oils - The lubrication of minute bearings of instruments has received too little attention over the past several years and problems arising with such have indicated a need for research and development in instrument bearing lubrication. Even though the operating conditions, in terms of temperature and oxidizing environments, are not as severe as other lubricant applications, other control needs require considerable attention. Indicating instrument and guidance instrument bearings, for example, gyroscope gimbal bearings are required to be as frictionless as possible. This means that only enough lubricant should be used not to flood the system, otherwise the lubricant will form varnish or oil insolubles which are capable of interfering with the bearing operation. The smaller the instrument ball bearings are that operate at thousands of revolutions per minute, the greater the lubricant problem. Extreme caution must be taken relative to the condition of the oil and the environments in which the oil is used. Considerable bearing failure has been experienced because of varnishing, and the overheating of bearings.

In applications where long term reliability is desired from antifriction bearings operating at high rpm's and where a liquid lubricant is necessary, it is essential to deoxygenate the lubricant, and use a completely oxygen free atmosphere in the bearing area. Considerable effort has shown that varnishing is induced by minute quantities of absorbed air in the oil or in the surrounding environment, causing oxidation of the lubricating thin film.

During 1960, a high temperature instrument oil formulation was derived. This oil covers a temperature range of -65°F to 400°F and is composed of a methyl chlorophenyl silicone oil with dibutyl tin sulfide as an additive. A military specification is being prepared for the temperature range of -65°F to 400°F . This instrument oil will not solve all instrument lubrication problems but it will aid instrument bearing lubrication at some higher temperature than those presently qualified under MIL-L-6085A which covers a temperature range of -65°F to 250°F .

We shall now consider the semi-solid lubricant materials commonly referred to as greases. High temperature greases (up to 600°F) are now available. Organic thickeners and synthetic organic fluids are utilized in formulating greases operable from -100°F to $+600^{\circ}\text{F}$, however, no individual grease is capable of operation over the entire temperature range without considerable limitations being placed upon its performance life. Considerable research and development work is needed to advance the state of the art to provide for greases and grease-like materials usable in various aerospace environments and operating conditions expected in advanced Air Force weapon systems. These lubricating greases will provide a highly reliable capability for long term operation (500 hours minimum) under conditions such as is shown in figure 8. The new and improved materials resulting from this research are intended as general and special purpose greases for lubricating control systems, gear boxes, gimbal rings, rocket control devices, generators, inverters, actuators, advanced electric motors, and other subsystems. The knowledge gained from previous efforts concerning the basic factors involving the formation and stability of grease-like colloidal gels are being applied to the development of new and improved grease structures and formulations. In order to provide for special purpose greases for use in advanced weapon systems several approaches are being followed.

Thickener Materials - A complete and comprehensive investigation is being made of organic, semi-organic, and inorganic materials, which melt above 700°F , for use as high temperature grease thickeners. Figure 9 shows the more promising organic materials which are under investigation, namely, the hydantoins, ammelines and the imides. The aluminum complex of phthalimido benzoic acid is one of the more promising imides, and will undergo further investigation, under high temperature-heavy load conditions. This thickener system has a melting point above 1200°F .

A study is being made of special surface modification techniques as shown in figure 10. Greatly improved greases with high temperature shear stability will result from the use of thickeners prepared by these special techniques. Carbon blacks, silicas, glass fibers, and metallic oxides are being investigated for suitability as grease thickeners.

Fluids - New base fluids and fluid blends with 700°F to 1000°F potential based on organic, metal-organic, and inorganic structures are being investigated in various thickener systems. The more promising base fluids are the polyphenyl ethers, silphenylenes, and high phenyl content silicones. Currently available fluids and those which will be available for grease synthesis in the future are listed in figure 11.

Additives - The potential performance of new and improved additives are being studied for their impartation of oxidation stability, wear resistance, corrosion resistance, and heavy load carrying capacity to grease formulations.

Summary - Figure 12 shows the current and future high temperature grease capability.

The currently available greases are either commercial or experimental.

The future requirements for high temperature greases will be for high speed applications primarily (1×10^6 DN Value). Apparently there will be a requirement for heavy load carrying grease capable of lubricating at high temperatures (600°F).

Figure 13 shows the heavy-load carrying grease capability.

Figure 14 shows the present and future high pressure (pneumatic) grease capability.

The lubricating grease requirements for the numerous present and future applications have been outlined. Much progress is being made in research and development, nevertheless, future aerospace requirements demand that a higher rate of progress be maintained. Those future requirements for high speed, high temperature, heavy load, radiation resistant, high vacuum, high pressure, and wide temperature range greases will be met through even more intense research and development programs.

Solid Film Lubricants

The aircraft industry is making wide use of the commercially available solid film lubricants. These films are being used in slow sliding bearings operating under loads of 2000 to 80,000 psi in the temperature range of ambient to 450-500°F. A typical application is the lubrication of outer control surfaces on aircraft which are practically impossible to lubricate with the conventional grease or oil lubricants. These films are particularly useful in inaccessible compartments since the parts can be coated prior to assembly and provide adequate lubrication for very long periods.

These films are generally composed of molybdenum disulphide and/or graphite as the lubricating pigment, and are bonded to the bearing surface with an organic resin binder. The mixture of pigment and binder carried in a solvent can be applied to the bearing surface by dipping, brushing, or spraying.

The resin binders are primarily of the phenolic or epoxy type with the epoxy resin generally preferred over the phenolic. These organic resins are the limiting factors for operation of these films above 450°F. At this temperature thermal degradation begins and wear life falls off rapidly when temperatures increase. The operating temperature of these films can be extended with the use of an inorganic binder such as a ceramic, to the oxidation temperature of the pigment. Molybdenum disulphide is stable to 750°F at which time severe oxidation begins. Figure 15 illustrates that ceramic bonded MoS_2 films show a considerable decrease in wear life at the lower or ambient temperature range compared to the resin bonded films.

The age of missiles and liquid gases as fuels have also generated the need for lubrication at the other end of the temperature scale, i.e., under cryogenic environments. At temperatures below -100°F most fluids turn to solids and like greases lose their lubricating capability. The use of solid film lubricants to lubricate moving parts under these conditions seemed natural. A recent program completed at the Directorate of Materials

and Processes was a study of commercial solid films under cryogenic conditions. As shown in figure 16, an 85 to 95 percent decrease in wear life could be expected in changing the environment from 70°F to the temperature of liquid nitrogen. No particular lubricant showed favorable wear life under these conditions. The postulated mechanism of failure was mechanical rupture of the bond between metal and film due to the initial thermal shock. It must be stressed that these films were not developed for cryogenic use but conceivably could be modified or developed further to operate satisfactorily for these environments.

Current R&D Efforts

The need for lubricants to operate above the temperature range of the grease and oil systems as well as the commercial films, has spurred the effort to develop a solid film lubricant for use at 1000°F. These efforts by the Air Force and other organizations have brought about lubricating pigments which are thermally and oxidatively stable to temperatures in excess of 1000°F. The Air Force has developed a ceramic bonded solid film which appears to meet the requirements of high temperatures and high loads, with low friction wear. The film is composed of lead sulphide as the lubricating pigment in combination with boric oxide, as the ceramic binder. This film exhibits both low friction and wear under loads to 60,000 psi and sliding speeds over 200 ft/min at 1000°F; wear life has exceeded all other films to date. This film suffers a serious drawback which has prevented it from being used in an operational capacity. This deficiency is the drastic decrease in wear life noted in tests conducted at temperatures below 700°F. Figure 17 points out the contrast with other film formulations with a decrease in wear life at higher temperatures. This phenomena is not readily explainable but much effort is being expended since the film has potential at temperatures of 1000°F.

One method to combat this deficiency has been an attempt to find an optimum mixture of MoS_2 and PbS which will provide adequate lubrication over the temperature range 80° to 1000°F. While this has improved the picture to a degree it still falls short of the necessary wear life for a successful film.

The work conducted by NASA on solid film lubrication has been similar to that of the Air Force. They have developed a ceramic bonded film composed of lead oxide and sodium silicate, which has shown good friction and wear values at 1000°F. However, this film follows the lead sulphide film in that an increase in friction and decrease in wear life is noted for lower temperatures. Recently, NASA, has turned to the use of solid films for lubrication of ball bearings as opposed to the use in plain journal or spherical bearings by the Air Force. The film used in these tests was the lead oxide with a mixture of various powdered oxides such as silicon dioxide, boric oxide, etc. Tests have indicated this film formulation shows great promise for temperatures up to 1250°F and sliding speeds to 10,000 fpm.

The Navy has also been conducting work on lubrication of ball bearings with a solid film lubricant. The work conducted at the Naval Air Material Center has been with a mixture of MoS_2 and graphite, bonded with sodium silicate. The primary interest here has been to design a bearing configuration suitable for use with a solid film lubricant. This has resulted in the reservoir theory whereas the bearing retainer contains reservoirs which provide the lubricant to the balls and races. The tests have been conducted at lower temperature, 350° to 700°F, but at high speeds of 10,000 rpm. The preliminary results indicate the bearings will operate for 20 to 30 hours under these conditions and may have the potential for successful operation at higher temperatures.

Recently, the scope of the Air Force research and development programs for solid films has been extended to cover new approaches and temperature ranges up to 1500°F, including operation in a vacuum at these temperatures. Special equipment has been constructed to provide testing at pressures of 10^{-6} mm Hg and temperatures of 1500°F, under various speeds and loads. This equipment is in operation now and some data have been taken at 1000°F in vacuum to 10^{-6} mm Hg. Figure 18 shows that mixtures of PbS and MoS₂ have given exceptionally better wear life under these conditions than either the PbS or MoS₂ films, or the mixture when run in air. The wear life for these films is short of the life needed in an operational system and work is necessary to develop a film with both the high temperature and vacuum capability. The data gathered under these conditions will be used as guides to screen materials for higher temperatures under vacuum environments.

The problem of finding pigments and binders which are stable under these high temperature conditions have necessitated looking at other types of coatings as possible friction and wear reducing compounds. A program is underway to find lubricating techniques which are usable to temperatures of 2000°F. The use of a porous substrate impregnated with precious metal alloys, glasses, or metals which form soft oxides have shown some promise. Another method tried under these conditions has been to run metal against metal without a lubricating medium, which has been promising.

As shown in figure 19, certain alloys such as the Haynes Alloy, Lt-1B, have shown essentially constant friction values for tests conducted in air over the temperature range of 1400 to 2000°F. Tests conducted in vacuum give higher friction values over this temperature range. These are only preliminary results but indicate the possibilities of successful operation with bearings containing types of materials for high temperature environments.

Fundamental research programs have been initiated to provide basic information concerning friction and wear. They will provide data to establish a foundation on which development programs can be conducted with a greater degree of success. More information is necessary for a better understanding of the mechanisms involved in friction and wear, and how to take advantage of the mechanisms to develop better solid film lubricants for unusual environments. Some of these programs involve studies at high sliding speeds between hard and soft metals, between soluble metals, and insoluble metals, and reactive and non-reactive metals to determine their effects on various properties of friction and wear. Why some solid film formulations exhibit poor wear life while others have excellent wear over a given temperature range is being studied from a phase or composition viewpoint. The effect of ceramic type binders and their role in affecting the lubricating pigment will be pinpointed.

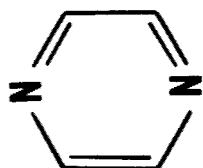
When the data from these programs is funneled into the development programs for solid films, it is hoped that sufficient basic data will be available to enable a formulation of a solid film lubricant for a specific application which will have a good chance for successful operation. These problem areas cannot be covered with a few programs in a short period of time but will take the combined effort of many organizations working closely to meet this challenge.

BIBLIOGRAPHY

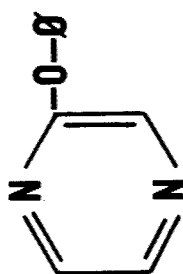
1. Behun, J.D.; Kan, P.T.; Naqui, S.M.; Gibson, P.A., "The Synthesis and Evaluation of New Base Stock Fluids for Gas Turbine Application", WADD TR 60-838, Part I.
2. Taylor, W.E.; Witt, E.R.; Thigpen, H.H., "The Synthesis and Evaluation of Aromatic Esters as Potential Base Stock Fluids for Gas Turbine Engine Lubricants", WADD TR 60-913, Part I.
3. Klaus, E.E.; Fenske, M.R.; Tewksbury, E.T., "Fluids, Lubricants, Fuels and Related Materials", WADD TR 60-898.
4. Chessick, J.J.; Zettlemoyer, A.C., "Basic Factors in the Formation and Stability of Non-Soap Greases for High Temperature Application", WADD TR 61-68.
5. Christian, J.B.; Griffith, J.Q., "Synthesis and Investigation of High Temperature Grease Thickeners", WADD TR 60-770.
6. Smith, R.K., "Development of High Temperature, Heavy Load-Carrying Greases", WADC TR 58-288, Parts II & III.
7. McCarthy, P.R., "Development of Grease for High Speed Ball and Roller Bearings", WADC TR 58-350, Parts I, II, & III.
8. Schwartz, A.A.; Broadly, H.R. Jr.; Norman, R.S., "High Temperature Instrument Oil", WADC TR 59-633, Parts I & II.

SPECIFICATION DESIGNATION	AMBIENT
APPLICABLE TEMPERATURE RANGE	
Mil-L-7808 D	-65° To 300°F
Mil-L-9236 B	-65° To 400°F
(Target) Mil-L-27502	-35° To 500°F

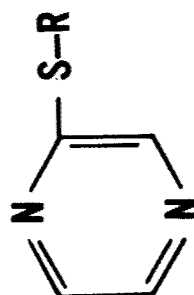
Figure 1.



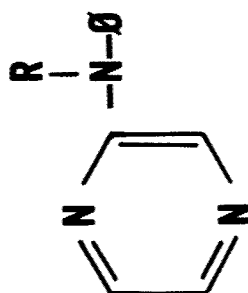
PYRAZINE



PHENOXY

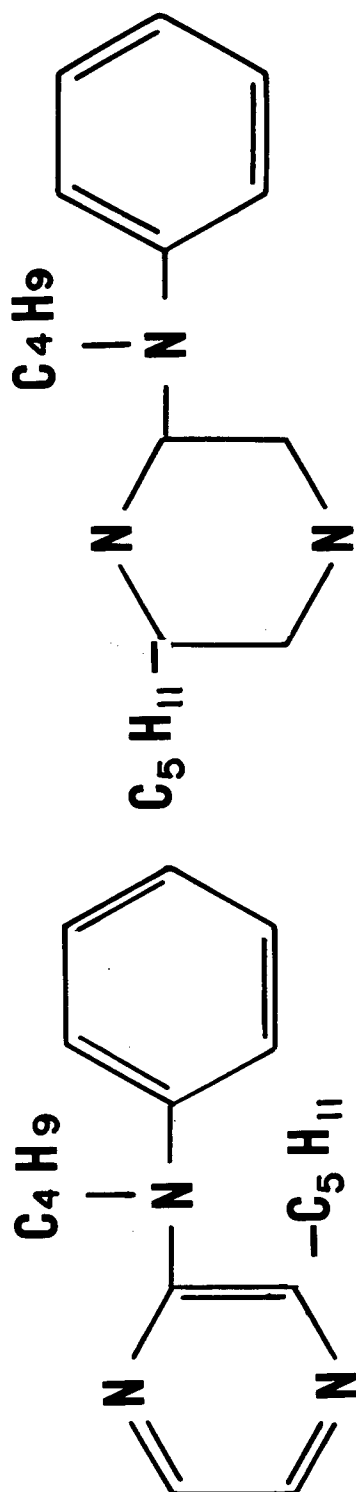


THIO



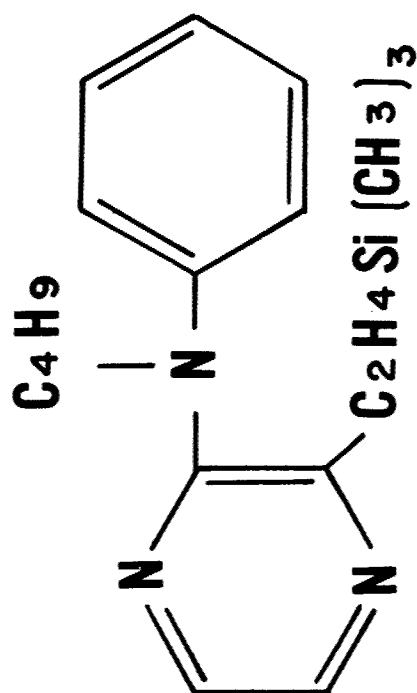
ANILINO

Figure 2.



BETTER FLUIDITY

Figure 3.



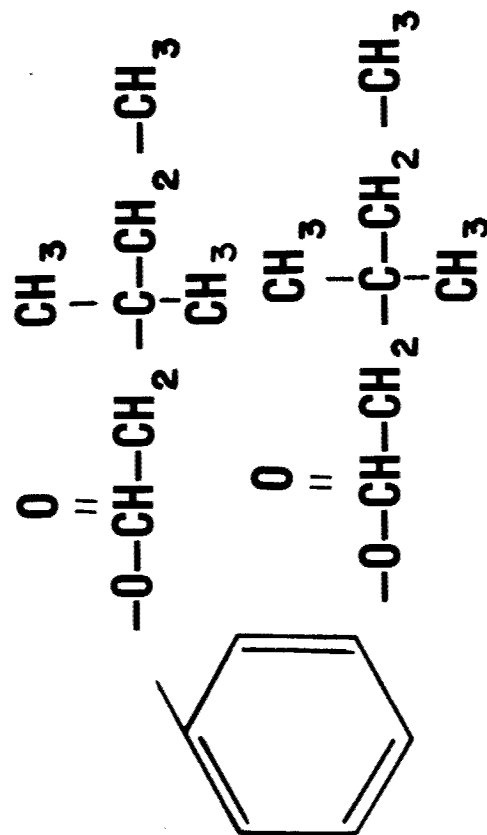
2,N-BUTYL ANILINO 3,ETHYL TRIMETHYLSILYL PYRAZINE

Figure 4.

THERMAL STABILITY (9 HOURS)									
COMPOUND	Micro B.P. °F	Test Temp. °F	Wt. Loss %	Color Change	Viscosity @ 100°F (Centistokes)		I R Change		
					Before	After			
2-n-Heptyl-5-n-nonyl-pyrazine	685	700	10.2	Very Slight	8.40	8.65	2.9	No	
MIL-L-9236 Base Stock	720	700	15.2	Slight	15.35	18.94	23	No	
MIL-L-9236 Formulation	720	700	15.1	Blackened	16.17	19.72	22	No	
2-(Di-n-hexylamino)-3-(5-nonyl)pyrazine	695	700	23.5	Darkened	20.14	72.39	164	Yes	
2-(N-Methylanilino)-3-(6-heptyldecyl)pyrazine	706	700	22.1	Darkened					
OXIDATION STABILITY (6 HOURS)									
COMPOUND	Test Temp °F	Color Change	Viscosity		Odor After	I R Change			
			Before	After					
2-n-Heptyl-5-n-nonyl pyrazine	500	Darkened	8.65	18.31	Slight	Slight			
MIL-L-9236 Base Stock	500	Darkened	15.35	55.06	Acrid	Yes			
MIL-L-9236 Formulation	500	Darkened	16.17	28.02	Acrid	Yes			
2-(Di-n-hexylamino)-3-(5-nonyl)pyrazine	500	Blackened	20.14	33.19	Slight	Slight			

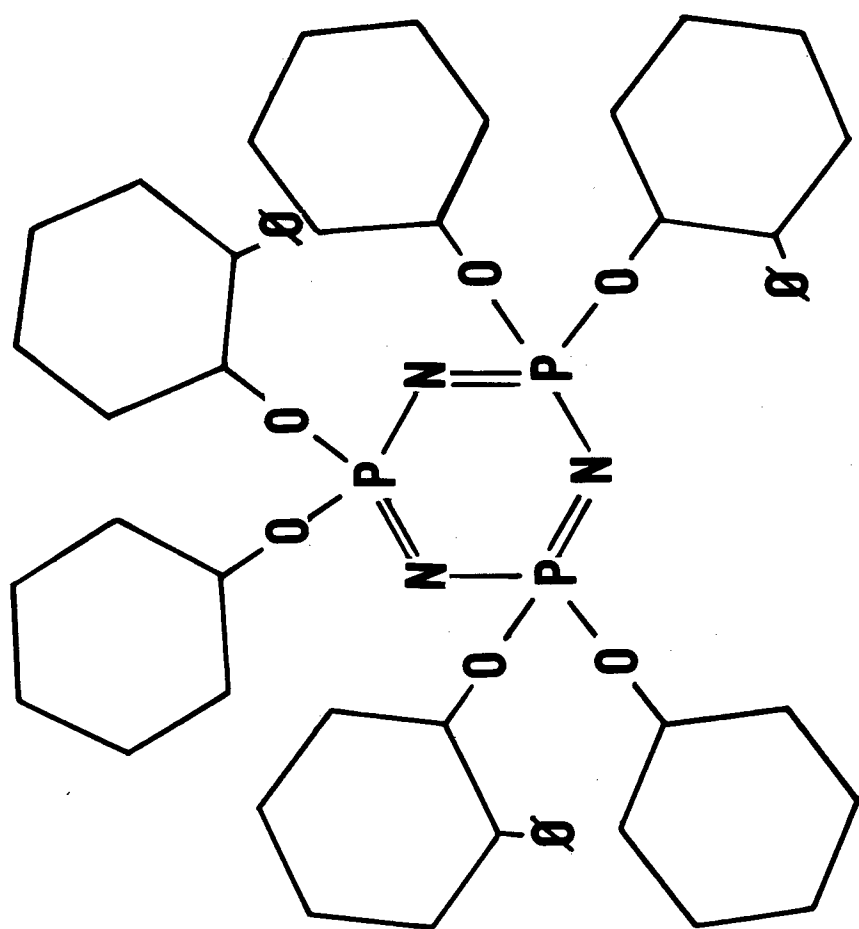
Figure 5.

POUR POINT -50°F



1,3,Recorcinyldiheptanoate

Figure 6.



TRIS [(Q-BIPHENYLOXY), (PHENOXY)] TRIPHOSPHONITRILE

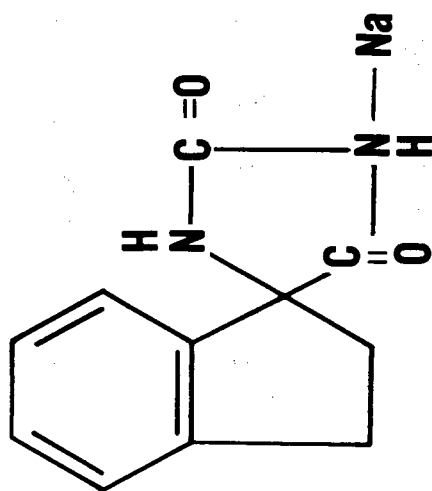
Figure 7.

FUTURE GREASE REQUIREMENTS

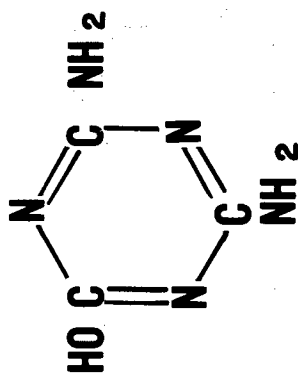
- **High Temperature Capability (600°F To 900°F)**
- **Wide Temperature Range (-100°F To +600°F)**
- **High Speed Capability (Up To 1×10^6 DN)**
- **Heavy Load Carry Capability (Mean Hertz Load Values Up To 75)**
- **Nuclear Radiation Resistance (Up To 1×10^{10} ergs/g Carbon)**
- **High Vacuum Capacity (To 10^{-7} mm Hg)**
- **High Pressures (Pneumatic Systems, Up To 4000 psi)**

Figure 8.

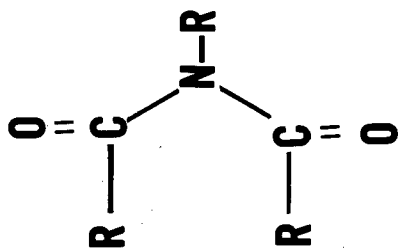
TYPICAL ORGANIC THICKENERS



Hydantoin



Ammeline



Imide

Figure 9.

SPECIAL SURFACE MODIFICATION TECHNIQUES



Resin Coating of Inorganic solids



Preparation of High Surface Area Inorganic Solids



ION Incorporation Techniques

Figure 10.

BASE FLUIDS

Current	Future
Silphenylenes	Polyphenyls
Silicones	Pyrazine Derivatives
Polyphenyl Ethers	Perfluoroaromatics
Silanes	Inorganics

Figure 11.

HIGH TEMPERATURE GREASE CAPABILITY PRESENT and FUTURE

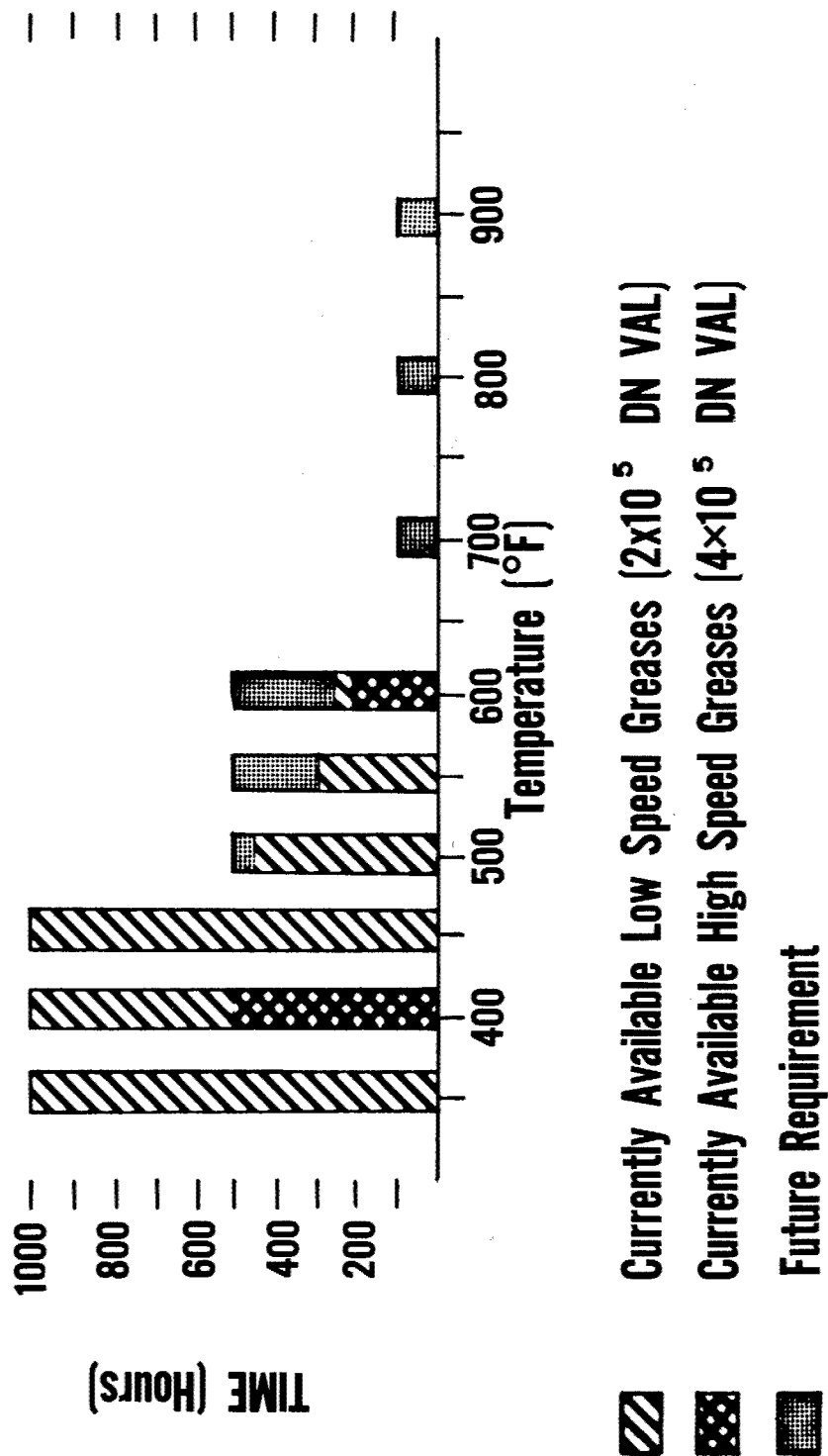


Figure 12.

HEAVY LOAD-CARRYING GREASE CAPABILITY PRESENT and FUTURE

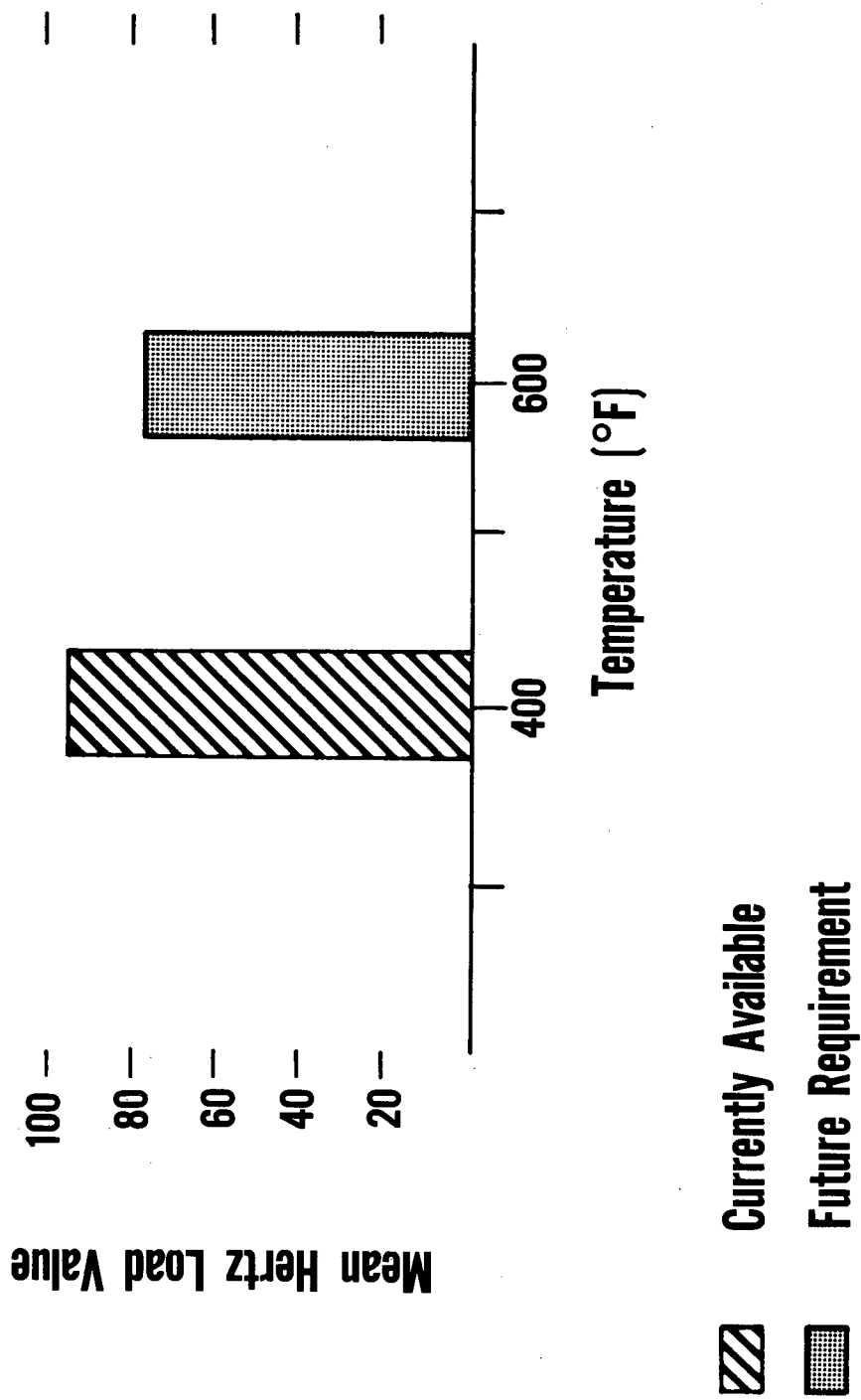


Figure 13.

PNEUMATIC GREASE CAPABILITY PRESENT AND FUTURE

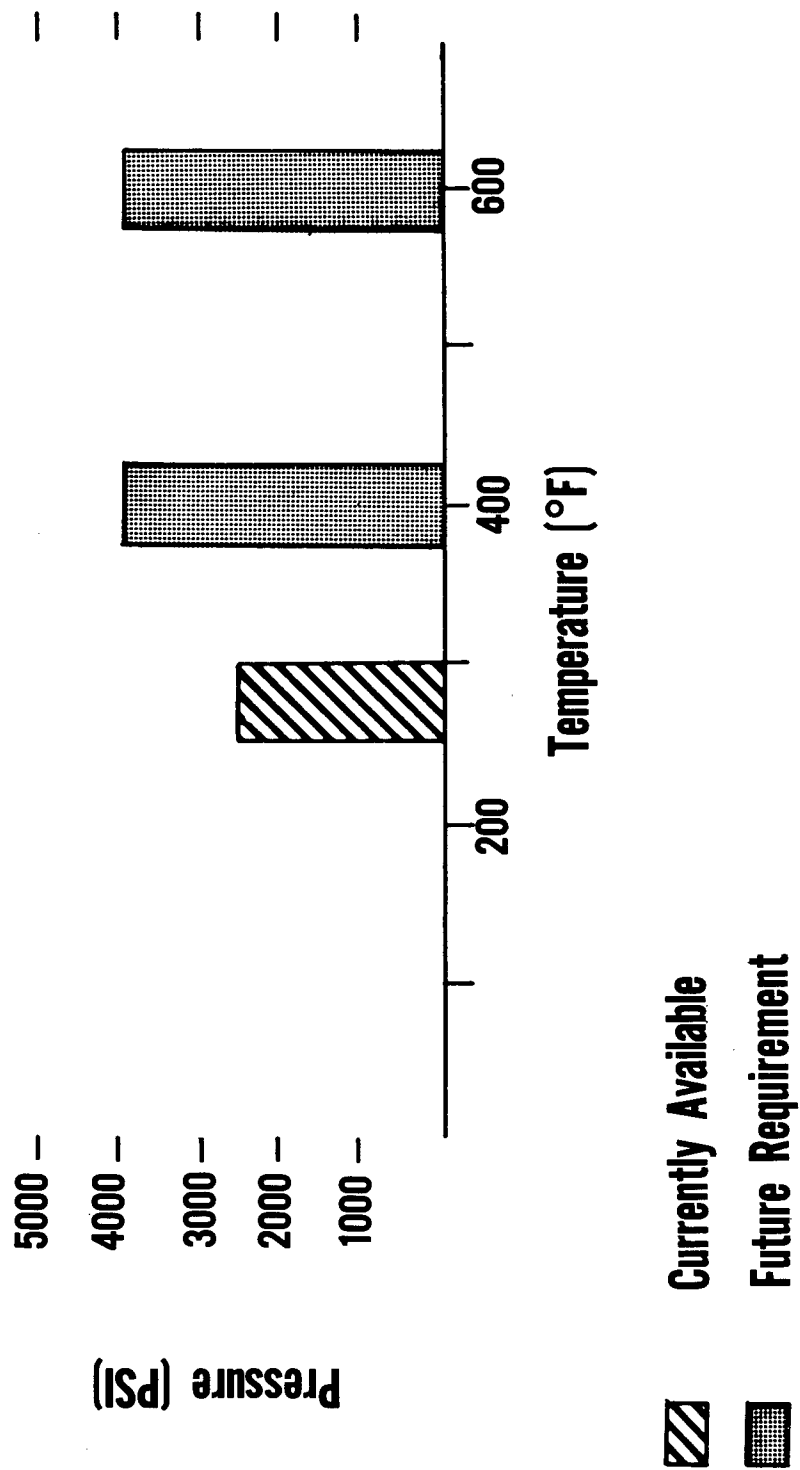


Figure 14.

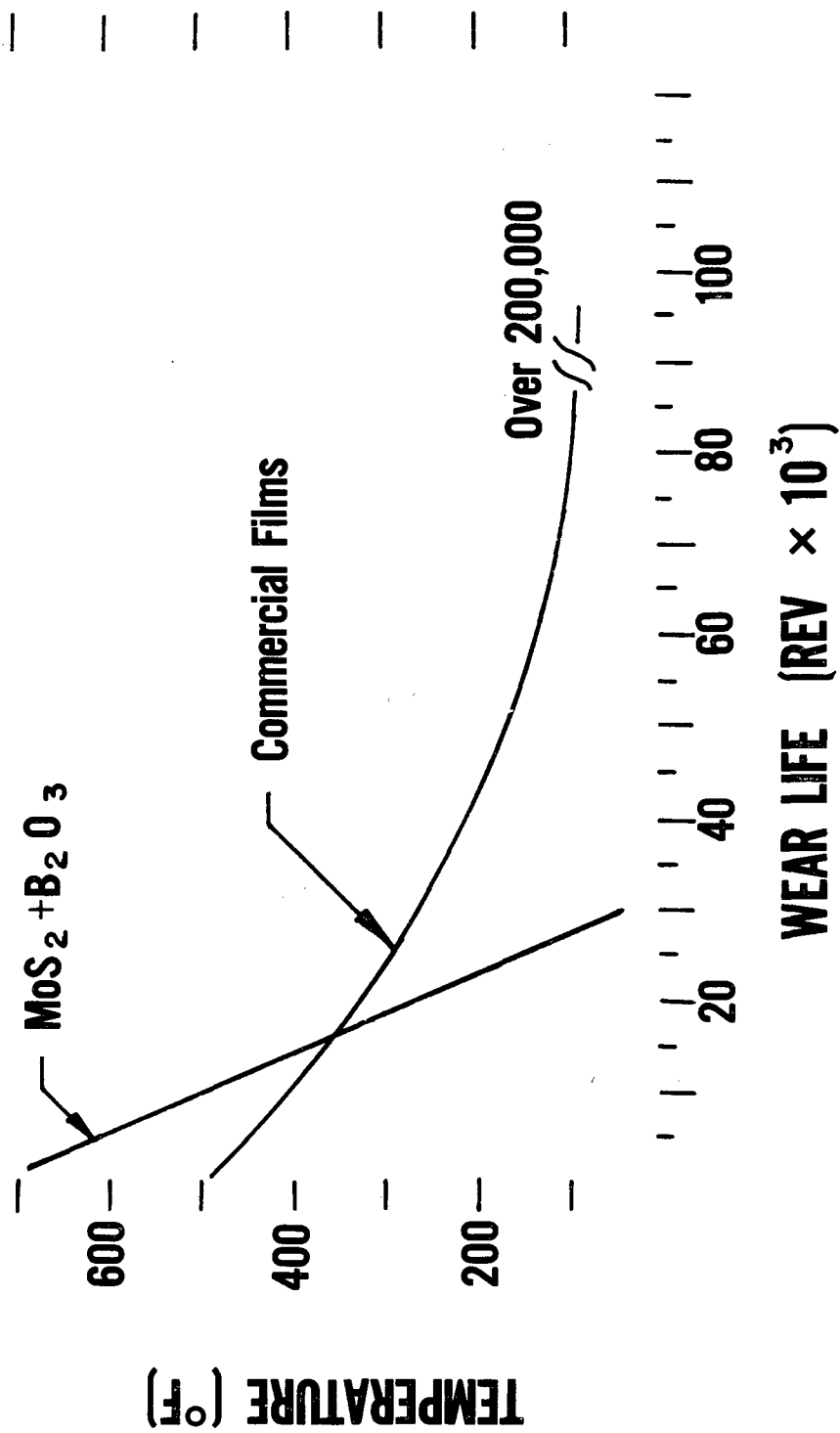


Figure 15.

WEAR LIFE IN MINUTES FALEX TESTER, 1000 Lb. LOAD

FILM A	AVERAGE, FOUR TESTS	AVERAGE LOSS in LIFE (%)
Room Temperature	206	88
Liquid N ₂	24	
FILM B		
Room Temperature	421	96
Liquid N ₂	17	
FILM C		
Room Temperature	296	97
Liquid N ₂	10	
FILM D		
Room Temperature	437	96
Liquid N ₂	20	

Performance Of Solid Film Lubricants In Liquid N₂

Figure 16.

WEAR LIFE of $\text{PbS-B}_2\text{O}_3$ FILM compared TO OTHER FILM FORMULATIONS

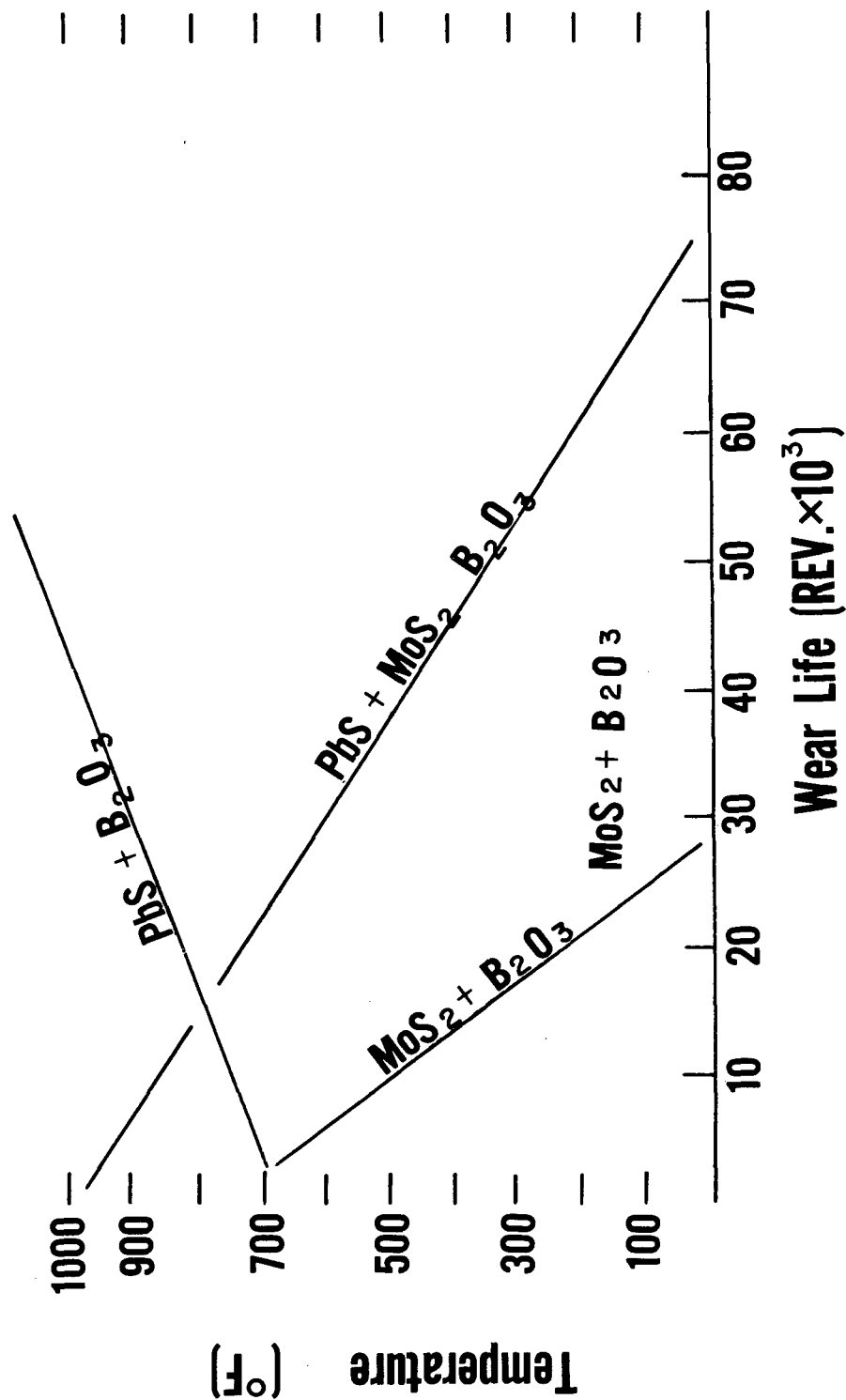


Figure 17.

WEAR LIFE of $\text{MoS}_2 + \text{PbS} - \text{B}_2\text{O}_3$ IN AIR and IN VACUUM (10^{-6} mm Hg)

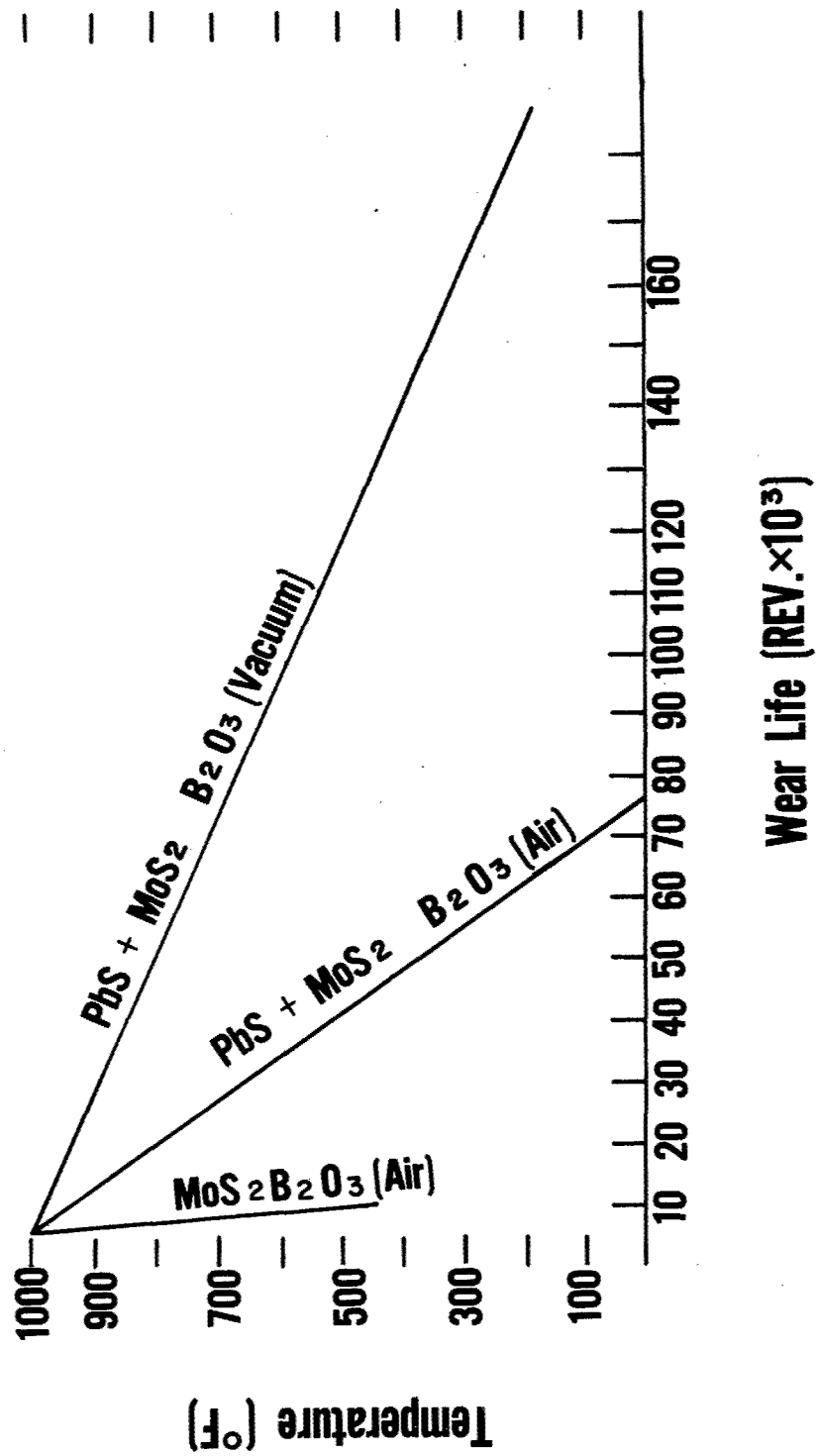
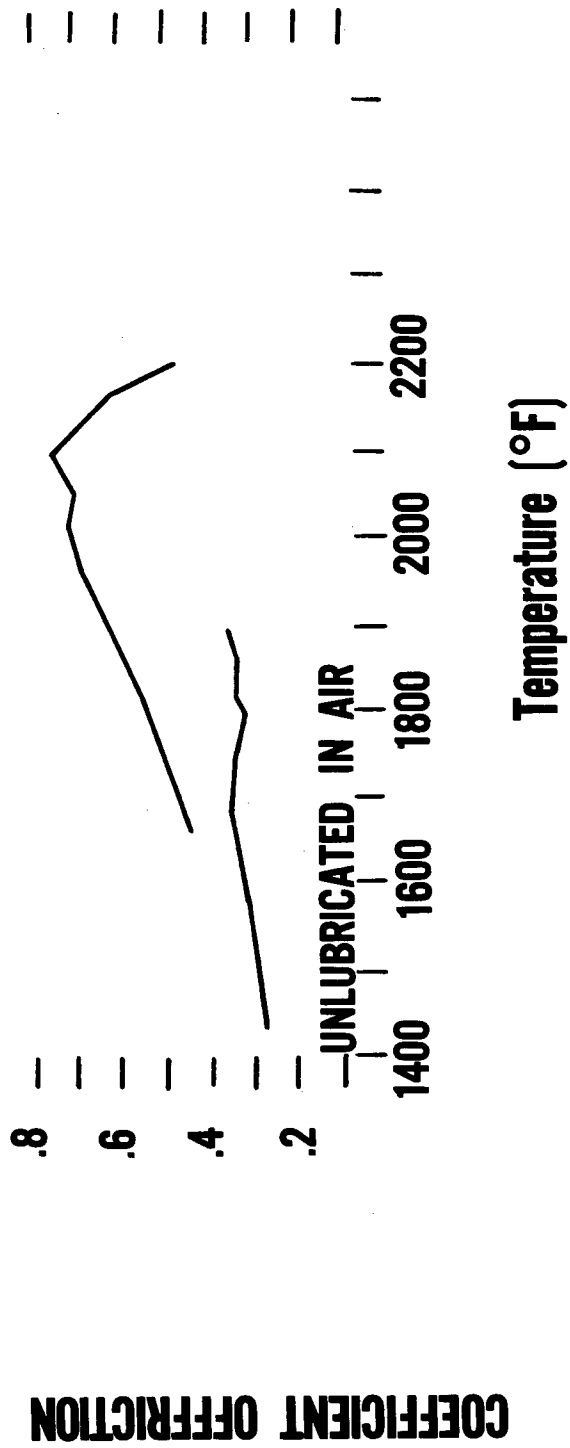


Figure 18.

UNLUBRICATED IN VACUUM (1×10^{-3} mm H₂)



Variation of Friction With Temperature, LT-IB Against LT-IB Unlubricated,
In Air And In Vacuum

Figure 19.

ADVANCED LUBRICATION TECHNIQUES

G.A. Beane

Directorate of Materials and Processes, ASD

The following discussion covers some of the more unconventional approaches being explored to meet anticipated lubrication requirements for liquid rocket engines and flight vehicle power equipment.

Propellant Lubrication

One of the more serious considerations in lubricating turbo pumps for liquid rocket engines is that of lubricant-propellant compatibility. This problem dictates the use of elaborate seals and, in the case of cryogenics, the use of lubricant heaters adds to the system's complexity. We should explore the possibility of completely eliminating the turbopump oil system by lubricating the gears and bearings with the propellants being employed in the system. Results of a recent program have revealed that this lubrication approach is entirely feasible for both bearings and gears within certain limitations. Tables 1 and 2 summarize the results obtained.

The bearing tests were all performed on 45 mm I.D. ball bearings at 25,000 RPM under a 330 lb thrust load for a one-hour duration when attainable. The ball and race materials were 440-C and the cages were glass supported teflon. In general, all of the propellants performed satisfactorily in the bearing tests except the amines (UDMH, EDA, N_2O_4) which were very poor. Based on simplified friction and wear screening test data, however, it is recommended that these propellants be evaluated further with other bearing materials such as berylco-25 and Ni or Co base alloys.

The gear tests were made with a 5-inch diameter gear and a 25-degree pressure angle. The tests operated at a pitch line velocity of 8000 fpm under loads of 500 ppi and 1000 ppi and 1000 ppi for durations of 15 minutes and 60 minutes respectively when attainable. The performance of propellant lubricated gears revealed that the same five propellants were generally satisfactory lubricants although not necessarily on the same gear materials. For example, while 440-C was a good material for RP-1, N_2O_4 , and IRFNA, it was found that the 9310 performed better in LH_2 and LO_2 . This is primarily attributed to the brittleness at cryogenic temperatures of 440-C and to a lesser extent nitralloy 135M. In no case did the amines perform well in gears; 440-C gears were especially poor, however, marginal performance could be attained under light loads when berylco-25 gears were used with the amines.

This program is being continued with the effort concentrated on finding gear and bearing materials which have good rolling and sliding characteristics in a 50 percent mixture of UDMH and hydrazine which is the fuel for Titan II.

Positive Displacement Lubrication

In the low horsepower range (<10 HP) a flight vehicle power source which appears competitive with the small gas turbines is the positive displacement engine. This type power source could be of the vane pump or piston type and driven by hot exhaust gases from either mono or bi-propellants such as hydrazine or hydrogen-oxygen. A stringent lubrication problem arises since the driving gas temperatures are around 1500°F and,

unlike a normal air-breathing engine, there is no air cooling cycle; thus the rubbing surfaces soon attain an equilibrium temperature approaching that of the driving gas temperature. The problem then boils down to providing a means of lubricating sliding surfaces under the conditions given in table 3.

These conditions pretty well rule out the use of conventional organic lubricants and thus various inorganic solid lubricants are being investigated. Various lubricants are not only being explored but various materials of construction as well, since the lubricant cannot be considered independently of the sliding metals. A tentative list of some of the structural materials and lubricants to be evaluated are shown in tables 4 and 5. Examples of some of the proposed materials of construction are molybdenum, nickel, and cobalt base alloys; titanium and chromium carbide nickel cermets; aluminum oxide, B_4C -TiB, and SiC- B_4C ceramics; graphite; and various flame platings. Examples of some of the lubricants that will be investigated are sulfur family binaries such as MoS_2 , PbSe, and Ag_2Te ; ternary compounds such as $MgSO_4$, $PbMoO_4$, or $PbCrO_4$; soft glasses; pure metals such as Cu or Ag; graphite, and certain polymeric materials which display unusually high thermal stability.

Lubricating Powders Entrained in Gas

In an attempt to raise the maximum temperature capability of high speed ball bearings various techniques were employed using lubricants other than conventional organic materials, which are inherently unstable at temperatures above 1000°F. Of the various techniques investigated the use of lubricating powders entrained in a gas carrier have demonstrated the best performance towards meeting the objective of 10 hours operation from room temperature to 1200°F, 50,000 rpm, and 100 lb load.

Table 6 lists the more successful test results obtained to date and the lubricants utilized. The bearings were cast and wrought, 20 mm bore and mostly constructed of either TiC or cobalt alloys. It was found that even the best of the single constituent lubricant powders did not perform well over the entire temperature range. Several lubricant powder mixtures were evaluated to find combinations which performed well throughout the temperature range. Molybdenum disulphide + phthalocyanine entrained in nitrogen and graphite + CdO carried in air were the most successful combinations evaluated. Such a lubrication scheme could be applied to the flight vehicle power systems for such concepts as Dyna-Soar or SLAM (a supersonic low altitude missile) where the equilibrium bearing temperatures would readily reach 1200°F or higher unless cooling was provided.

Gas Lubricated Bearings

Another approach to obtaining high temperature lubrication is the use of gas lubricated bearings. Ironically one of the reasons gas bearing lubrication is an attractive prospect for high temperature applications is that the viscosity of the lubricant (gas) increases with temperature, which means, all other things being equal, that higher loads can be supported as the temperature increases.

In addition to the high temperature advantage there are other desirable characteristics of gas lubricated bearings - particularly their complete stability to high radiation dosages, their increased load capacity at higher speeds, and their extremely low power requirement. Gas bearings have definite limitations and before any serious consideration is given to their utilization in hardware equipment one must first determine that the requirements are within the gas bearing capacities particularly with respect to load and gas flow.

There are several flight vehicle power applications involving light loads where one can envision a sufficient supply of gas to make the use of gas bearings appear feasible. For example, in a high mach ramjet there would be an abundant supply of high temperature, high pressure air; in a non air-breathing application where the flight vehicle power unit is driven by decomposition gases of a propellant such as hydrazine, there would also be a high temperature, high pressure supply of exhaust gas available. It is also conceivable that the self-acting bearing could be used in certain applications where the whole bearing environment could be enclosed and pressurized with only a small make-up bottle needed to handle small amounts of leakage.

To determine experimentally the maximum load carrying capacity of gas bearings under conditions representative of typical flight vehicle power equipment, the performance of various bearing designs at speeds up to 65,000 RPM and temperatures to 1500°F has been studied under contract. The results to date have shown that at least a 5-pound load can be carried on a 2-inch by 1.5-inch diameter bearing at all temperatures up to 1500°F and all speeds up to 65,000 RPM with gas flow rates slightly less than 5 pounds per hour at the extreme conditions of temperature and speed. These tests were conducted on flame plated Inconel-X bearings using nitrogen gas as the lubricant. Future plans are to extend the capability of the rig by building an all ceramic test bearing. This should permit operation at temperatures up to 2200°F with an oxidizing gas such as air as well as inert gases. In addition gases of widely differing viscosities and densities such as He, A, and CF₄ will be employed to study the effect of these properties on bearing performance and load carrying ability.

Liquid Metal Lubrication

There are certain types of power equipment, namely the closed loop space power equipment which must be lubricated with the working fluid itself. The schematic shown in figure 1 is a simplified illustration of the operation of a single loop closed cycle system. The working fluid (for example, mercury, potassium, or rubidium) is vaporized in a heat source such as a nuclear or solar boiler, the hot vapor is then expanded to drive a turbine which directly drives a generator; the exhaust vapor is condensed in a heat exchanger or radiator and pumped back into the heat source. These systems are designed to operate for long duration satellite and space vehicle applications. As one can well imagine, the use of a conventional oil system is prohibitive since adequate sealing cannot be provided for durations of 1 year or more. Consequently, the working fluid itself must be used as the lubricant. For example, a small portion of the liquid phase of the working fluid could be diverted to the bearings after leaving the pump. The temperature of the liquid going into the bearings would be somewhere between 500°F and 1200°F depending on the system design and the particular working fluid being used.

The relative performance of various liquid working fluids in journal bearing is being investigated with particular emphasis on potassium and rubidium. The test conditions and objectives of this investigation are given in table 7.

The overall objective is to provide a means of satisfactorily operating under typical hardware conditions for long durations. The results to date have been preliminary in nature. The test rig and its support system has been checked out on liquid potassium and appears to be operating satisfactorily. Tests using various test bearing sizes and designs will be evaluated next. The test rig is constructed of stainless steel. The test bearings consist of a chrome plated stainless steel shaft with bearing sleeve inserts of various materials such as aluminum bronze, silicon bronze, graphite, etc. Aside from the potential corrosion problem and the problem of bearing performance using these liquid

metals another problem which could prove to be a serious limitation for extremely long life (10,000 hours or more) is that of erosion, particularly with a high density liquid metal such as mercury.

Vapor Bearing Lubrication

An alternate method of accomplishing closed loop bearing lubrication is to utilize a small portion of the high temperature, high pressure vapor phase of the working fluid as it leaves the boiler. In other words, vapor bearing lubrication is a complicated cousin of gas bearing lubrication. Some of the additional problems of lubricating with an alkali metal vapor rather than a gas are (1) corrosion and the associated problems of jamming, scarring, and clogging resulting from corrosion products debris, and (2) liquid condensation occurring within the bearing due to transient temperature and/or pressure changes; it is not certain what effect this condensate would have, although it is probable that the presence of liquid in the bearing would destroy the supporting gas film.

Despite these anticipated problems there are several important advantages that could be realized by using vapor bearings; particularly those of reduced erosion and wear which should aid in attaining long life. Less cooling would be required, since the bearings could be operated at approximately the same temperature as the vapor (from 1200°F to 1800°F depending on the fluid and system). Other advantages, particularly with respect to long life operation, are those of low friction and low horsepower consumption.

There are two other lubrication schemes which appear worthy of additional research. One of these is magnetic bearings, that is, bearings supported by a magnetic field. Although there are several operational disadvantages with magnetic bearings namely low load carrying capacity and instability; however, with sufficient development there would be some distinct advantages, particularly at cryogenic temperatures where power losses would be very low.

The other type is electrostatically supported bearings. Electrostatic bearings offer a possible solution to the lubrication problem associated with electrostatic generators. The high vacuum of space is an ideal environment for operating an electrostatic generator, but it poses a severe lubrication or sealing problem. If, however, electrostatic bearings could be used, the advantages would be obvious. Not only is an abundance of electrostatic electricity available, but the high vacuum of space becomes a definite asset.

In summary there are several applications in which the use of organic lubricants create definite limitations to the system. There are, however, unconventional lubrication techniques which, if sufficiently explored and developed, could unveil capabilities presently far beyond today's state of the art and in some cases even beyond ones imagination. To accomplish this unveiling, the "Conventionalism Barrier" must be broken and new lubrication techniques explored with uninhibited vigor.

Government sponsored research has only scratched the surface. There are still many challenging research avenues which need exploration. We sincerely hope that the challenge will be accepted.

LIST OF ABBREVIATIONS

UDMH	Unsymmetrical dimethylhydrazine
EDA	Ethylenediamine
N_2O_4	Nitrogen tetroxide
RP-1	Low-cut hydrocarbon, essentially kerosene
IRFNA	Inhibited red fuming nitric acid
LH_2	Liquid hydrogen
LO_2	Liquid oxygen
N_2H_4	Hydrazine

REFERENCES

1. Butner, M.: "Propellant Lubrication Properties Investigation" WADD TR 61-77.
2. Amateau, Krause, Orcutt, Glaeser, Allen: "Development of Lubricants for Positive Displacement Power Sources from 1200°F to 1500°F," Progress Reports Nos. 1 & 2, Contract AF 33(616)-7568, Directorate of Materials and Processes.
3. Wilson and Gray: "The Development of Lubricants for High Speed Rolling Contact Bearings Operating over the Range of Room Temperature to 1200°F," WADD TR 60-732, January 1961.
4. Macks, F : "Gas Lubrication of Radial and Thrust Bearings at Very High Temperatures, High Speeds and Low Lubricant Flow Rates," WADD TR 61-83, February 1961.
5. Contracts AF 33(616)-6860 and AF 33(616)-8328 "Liquid Metal Lubrication of Journal Bearings", Directorate of Materials and Processes.
6. Contract AF 33(616)-8082, "Metal Vapor Lubrication of Thrust Bearings", Directorate of Materials and Processes.

TABLE 1
PROPELLANT LUBRICATED BALL BEARINGS

<u>MATERIALS</u>	
RACES AND BALLS: 440-C	
CAGES: GLASS SUPPORTED TEFLON	
<u>PERFORMANCE</u>	
<u>GOOD</u>	<u>POOR</u>
RP - I	EDA
LH - 2	UDMH
LO ₂	N ₂ H ₄
N ₂ O ₄	
IRFNA	

TABLE 2
PROPELLANT LUBRICATED GEARS

PROPELLANT	<u>PERFORMANCE</u>		
	<u>GOOD</u>	<u>FAIR</u>	<u>POOR</u>
RP - I	NIT. 135 M 440 - C 9310		BERYLCO 25
LH ₂	9310	NIT. 135 M 9310 vs. NIT. 135 M	440 - C BERYLCO 25
LO ₂	9310 NIT. 135 M	440 - C	BERYLCO 25
N ₂ O ₄ IRFNA	440 - C		
EDA		BERYLCO 25	440 - C
UDMH		BERYLCO 25	440 - C
N ₂ H ₄		BERYLCO 25 BERYLCO 25 vs. 440-C	440 - C

TABLE 3

POSITIVE DISPLACEMENT LUBRICATION REQUIREMENTS

MOTION: RECIPROCAL AND ROTATIONAL SLIDING
 SPEED: UP TO 80 FT/SEC
 TEMPERATURE: UP TO 1500°F
 LOAD: UP TO 50 PSI
 ENVIRONMENT: INERT, REDUCING, OR OXIDIZING
 ENVIRONMENTAL PRESSURE: 0.5 TO 1000 PSIA
 DURATION: UP TO 300 HRS.

TABLE 4

CANDIDATE STRUCTURAL MATERIALS

ALLOYS	CERMETS	CERAMICS	FLAME PLATINGS
Mo Base	TiC - Nickel	B ₄ C - TiB	Al ₂ O ₃ on Hastelloy W
Ni Base	CrC - Nickel	SiC - B ₄ C	
Co Base			

TABLE 5

CANDIDATE LUBRICANTS

SULFUR FAMILY	TERNARY COMPOUNDS	PURE METALS	GRAPHITE	POLYMERIC MATERIALS
Mo S ₂	MgSO ₄	Cu		
Pb Se	Pb Cr O ₄	Ag		
Ag ₂ Te	Pb Mo O ₄			

TABLE 6

UNCONVENTIONAL BALL BEARING LUBRICATION

<u>BEARINGS</u>		
20 mm bore TiC or Cobalt Alloy		
<u>CONDITIONS</u>		
30,000 RPM, 100 lb thrust, 10 hours 80°F through 1200°F		
<u>LUBE</u>	<u>CARRIER</u>	<u>PERFORMANCE</u>
MoS ₂	Nitrogen	High Friction in 800 to 1000° F Range
MoS ₂ - PCH ₂	Nitrogen	Good
Graphite - CdO	Air	Good

TABLE 7

LIQUID METAL LUBRICATION

TEMPERATURE: ROOM TEMPERATURE OR MELTING POINT UP TO 1200° F

BEARING SIZES: L/D = 2 OR LESS; DIAMETER = 1.0 IN.

BEARING SPEEDS: UP TO 36,000 RPM

BEARING DESIGNS: SELF - ACTING, EXTERNALLY PRESSURIZED

RADIAL LOADS: UP TO 100 LBS

LUBRICANTS: MERCURY

POTASSIUM

RUBIDIUM

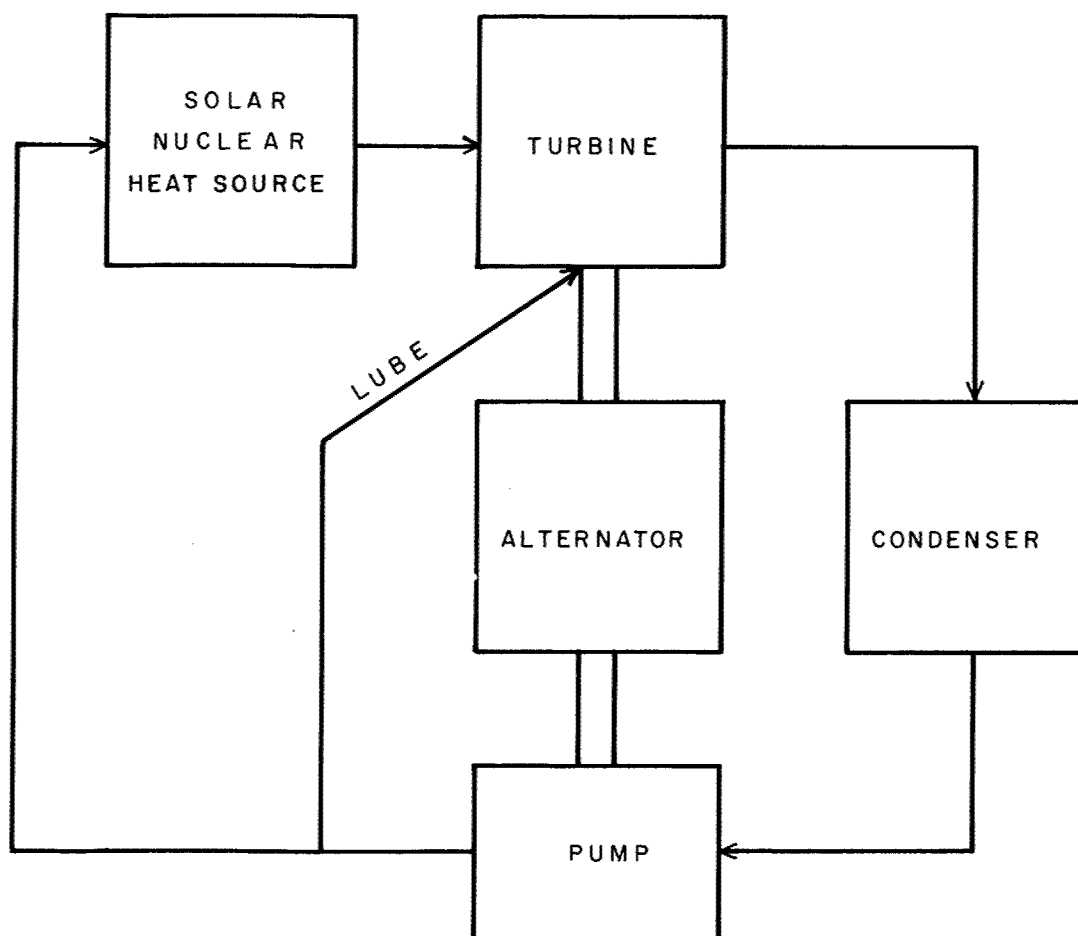


Figure 1.

ELASTOMERS

Chairman	Mr. J. M. Kelble
Speaker	Mr. R. G. Spain
	Mr. W. R. Griffin
	Dr. W. E. Gibbs
Panel Member	Mr. R. E. Headrick

ELASTOMERS

Dr. W.E. Gibbs

Mr. W.R. Griffin

Mr. R.G. Spain

Directorate of Materials and Processes, ASD

Introduction

The successes by the United States since our last Materials Symposium in 1958, in designing and launching all sorts of manned and unmanned aerospace vehicles could conceivably lead one to believe that all the Air Force problems associated with elastomeric materials have virtually been solved. Unfortunately, or fortunately since this would mean that most of us here today would be out of a job, as the case may be, the requirements for vastly improved elastomeric and compliant materials are still with us. Indeed, elastomers have been, and are still, one of the most environment sensitive of any of the materials of construction and the requirements and environments wherein elastomers are needed to perform for advanced design flight vehicles have become even more stringent. The temperature and pressure range has been even further expanded, the list of fuels, oxidizers, and fluids needing resistant elastomeric seals and sealants is even greater and more awesome, and last but not the least, the research for elastomers resistant to the radiation spectrum has become no less intense.

Appraising elastomer research efforts for the past ten years we could effectively divide the decade into two equal periods. Progress during the period from 1951 - 1956 was most notable and we saw the maximum operating temperature limit for organic elastomeric polymers raised from 250°F to 600°F. Accompanying the significant improvement in thermal stability were vast improvements in chemical resistance and a five to ten fold improvement in resistant to high intensity radiation. Of course, it was recognized even at this time that in so far as temperature stability, 600°F was the ultimate for organic elastomeric polymers. In the ensuing years, 1956 to 1961, no new high polymers have been discovered which have significantly advanced this temperature limitation. All of the meaningful advancements that have been made during the second five year period, in so far as temperatures above 600°F, have been made through the use of design innovations or through the use of unusual resilient composite systems of materials. This does not mean to say that the polymer chemists and rubber industry have been completely stagnant during this time. On the contrary several new hydrocarbon elastomers have reached fruition, including the cis-polyisoprenes, cis-polybutadienes, ethylene-propylene copolymers, and new versions of polyurethanes, silicones, and fluorocarbons, which represent real contributions to the science. Unfortunately, except for a few isolated cases these elastomers do not have sufficient thermal, chemical and radiation stability to fulfill current and future critical Air Force requirements.

As a means of setting the stage for the principal phases of Air Force elastomer research some of the more critical applications and environments in which elastomers will be expected to perform reliably for sustained periods of time are summarized below:

Figure 1. Applications of Elastomers in Aerospace Vehicles

Figure 2. Aerospace Environments

The main part of the program for the Elastomers Panel is divided into three areas portraying a logical, well planned elastomer research program necessary to obtain solutions to the critical problems at hand. The three areas are Synthesis, Characterization, and Engineering.

Synthesis covers the long range program of the Air Force for the preparation of new polymers which may be organic, semi-organic, or inorganic. Primary emphasis will be on polymeric materials which behave in accordance with accepted definitions of elastic behavior.

The second phase, Characterization, is perhaps the least understood and until very recently has received the least attention in research programs for new elastomeric materials. The current approaches used in bridging the gap between the polymer chemist and the elastomer engineer are presented. The steps are outlined whereby the scientist studies the chemical and physical nature of polymers, and transforms them into elastomeric vulcanizates through the use of proper cross-linking agents. The chemical, physical and mechanical properties are investigated in sufficient detail to provide the engineer a feeling for the end use capability. Also, information is fed back at this stage to the synthesis program on any chemical, physical, and mechanical deficiencies in new polymers.

Lastly, Engineering will concentrate on applied research efforts to provide elastomeric materials suitable for fabrication into components as outlined in figure 1 and resistant to the environments detailed in figure 2. One principal difference in this phase is that many of the materials used do not conform to the classical definitions normally assigned to elastomers. Many of the materials would better be described by such words as "resilient," "compliant," "composite systems of materials." In fact, the term "elastomer" as used by the elastomer engineer would better be redefined as any material of construction, organic or inorganic, metallic or nonmetallic, composite or unmodified, used alone or in combination, which is used where an elastomer would normally be used if the environment were favorable.

Synthesis

The synthesis of elastomeric compounds for use in extreme environments has been the subject of considerable Air Force interest over the past several years. The principal problem areas have been (1) thermal stability, (2) solvent resistance, (3) retention of required mechanical properties over wide ranges in temperature, and, (4) radiation resistance, as well as some others.

Certainly significant contributions have been made toward solving these problems. The advent of the fluorocarbon elastomers, for a time, appeared to cope well with the thermal stability requirement. The successive development (figure 3) of the fluoroacrylates 1F4, 2F4, the fluorocondensation polymers, the fluorosilicones, and finally the Viton and Fluorel type fluoroelastomers have pushed the temperature limits increasingly upwards. In a like manner the solvent resistance area was systematically attacked. Elastomers are now available which do a commendable job in contact with conventional jet-engine fuels, hydraulic fluids, and others. Some progress has been made toward the retention of strength at elevated temperature, most notably with the oxide cured acrylate copolymers, as well as resin-cured butyl and ethylene-propylene copolymers. Some progress has also been achieved in the case of elastomers resistant to ionizing radiation, as well as for other lower energy radiation.

However, the progress made thus far has been overshadowed by the increased requirements placed by the design people responsible for tomorrow's weapon and support systems. Whereas a few years ago the maximum temperature limits were 300°F, then 500°F, the thermal limits are now in the over 500°F range and will soon approach 2000°F in some applications. Formerly elastomers were sufficiently resistant to solvents if they showed minimal deterioration in jet fuels and hydraulic fluids. Now the Air Force is concerned with seals for nitrogen tetroxide, and chlorine trifluoride as well as liquid fluorine. Former concern was with elastomers retaining some degree of flexibility and elasticity at -65°F. Now we are entering cryogenic applications for seals and some other application. At the high temperature end, elastomeric compounds are required showing better retention of properties at ever increasing temperatures.

In order to meet these increased requirements, the Polymer Branch and the Elastomers and Coatings Branch of Directorate of Materials and Processes have pursued a program involving both short-range and long-range objectives. The short-range programs will be covered in more detail in the latter portion of this paper.

In the long-range programs, attempts have, and are, being made to study new classes of compounds to gain more knowledge about their properties. In particular, we have devoted some fair degree of effort in systematically studying the formation of polymers from organic, semi-organic, and inorganic compounds. Much of the organic work is devoted to structures which are believed to have a high inherent stability. For example: poly(aromatics), poly(heterocyclics), and polymers with cyclic or ladder type units. These are schematically shown in figure 4. The results of several programs have indicated that the aromatic systems particularly have a high inherent stability. Benzene was found to be stable in the vapor phase to over 1000°F. It is anticipated that other aromatic systems will also retain or improve upon this limit.

The types of polymers of interest to us here differ radically in many cases from the types of structures one commonly thinks of as an elastomer.

One area of work which is familiar to many of you is the polyperfluoroamidine system of figure 5. This system has a relatively good thermal stability, at least when compared with conventional elastomers. Furthermore, it has the unique feature that even after a significant portion of the material has degraded and volatilized the residue is still elastic. The principal disadvantage in the past with this system has been that following the original synthesis, a pyrolysis reaction, the material was highly cross-linked and hence non-processible. An alternate route has been found which again makes the system more attractive. By this method a prepolymer is obtained from a low temperature reaction which may be formed into the desired shapes, then heated at higher temperatures with the loss of ammonia to convert it to the polyperfluoroamidine (figure 6). This polymer apparently retains its enhanced thermal stability, but with the feature that it now approaches a useful material.

During the past year or so a good deal of work has been done on polyaromatic structures. This work was devoted primarily to high temperature fibrous materials, and therefore the polymers are rather rigid structures. Particularly the benzimidazole polymers of figure 7 and others of a similar structure have been found to be quite heat resistant. It is possible that these structures may be modified to yield more compliant materials without too much of a sacrifice in stability. It is also interesting to note that these materials also retain a fair degree of original mechanical properties at high temperatures.

The results of other long-range programs have been disappointing with regard to elastomers. In the semi-organic and inorganic areas very little promise has been found. The materials that have been synthesized are of rather low molecular weight, but it is rather unlikely that significant elastic properties will be realized even when higher molecular weights are obtained.

It has formerly been the general feeling that a gain in high temperature properties should not be accompanied by a significant sacrifice in properties at room temperature. In other words, we have looked at stretching out the plateau of rubber-like elasticity over wider temperature ranges rather than shifting this rubber-like region to higher and higher temperatures with about the same breadth of the elastic region. Perhaps we will now have to concentrate on materials with higher glass transition and crystalline melting temperatures to even approach the required higher performance temperatures.

In addition to the work on synthesis briefly outlined above, some effort has also been initiated on the mechanical properties of representative classes of elastomers to obtain more information about the requirements for retention of strength at higher temperatures, as well as more detailed information on a better explanation of the parameters operating at normal temperatures. Although this work is quite long range it is expected to yield very important information for the future design of compliant materials.

It is the opinion of many concerned with research for new elastomeric compounds, that the design of new elastomers is considerably more difficult than many other forms of polymers such as structural plastics, coatings, even fibrous materials. This is due to the particular combination of properties that elastomers must possess in order to function. In some applications polymers function very well by doing little more than occupying space. Also, they may be filled with types of highly reinforcing materials. These reinforcing materials may actually contribute the necessary strength properties for the application. In elastomers, however, this is not true. The elastomeric compound must show a balanced combination of resilience, modulus, ultimate tensile and elongation coupled with fluid or solvent resistance, generally over a wide temperature range. It is true that for some applications an elastomer need only possess a minimum in perhaps one or two of these properties, but then the other properties must be at a maximum and be retained for considerable times.

As can be seen, the program is not very extensive at this time, particularly regarding synthesis effort. The reason for this is the lack of good ideas for potentially useful systems. Marginal increase in thermal stability coupled perhaps with more significant gains in properties, may be found with better compounding technology for the present day fluoroelastomers. But larger gains in stability and serviceability will come only from new elastomer systems. For the long range programs minor modifications to fluoroelastomers are not of interest. New polymer structures or synthetic approaches to potentially useful polymer structures, which can offer something in stability beyond the fluoroelastomers are of prime consideration.

Characterization

The word elastomer, for purposes of this phase, refers to a compounded vulcanized elastomeric polymer. By this definition the elastomeric polymer or simply polymer is the basic raw material, which is modified or transformed into an elastomer by the addition of vulcanizing agents, reinforcing fillers, and stabilizers, usually followed by the application of heat and pressure to mold a specific shape.

You will notice from the discussion of the previous phase, that we are rapidly pushing beyond the thermal and chemical stability limits of conventional polymeric structures. Improved polymers will have different and perhaps very unusual structures, but all will most likely have one feature in common. These materials will be very expensive in terms of money and research time. The price for initial samples of these materials is enough to make one almost forget the need for improved elastomers. Excluding the cost of research to the preparation stage, several thousand dollars per pound is not uncommon. The monomers must often be synthesized by new and unrefined procedures and contribute heavily to this high cost. You can appreciate that new polymers are prepared in small quantities, usually about ten to fifteen grams.

This quantity is sufficient for the initial measurements made by the polymer chemist. However, the situation often arises in which the polymer is worthy of further evaluation as a compounded vulcanized material. The preparation of a vulcanizate and its characterization are usually outside of the polymer chemist's immediate interests and capabilities. On the other hand, few facilities exist where such small quantities of polymer can be compounded, vulcanized into test specimens and used to obtain meaningful data. The obvious economical advantages of working with these initial samples on a micro-compounding scale were recognized by the Air Force and the Elastomers Section has built up a capability in this area. The remainder of this phase will describe the characterization process, the specialized equipment, and problem areas involved.

The purpose of characterization is twofold. First the chemical, physical, and mechanical behavior of possible new elastomer materials must be defined per se and secondly, information and corrective recommendations for deficiencies or undesirable properties must be returned to the synthesis program. This feedback of information is very important. Polymer programs, while directed toward newer and more stable polymeric structures, must also produce useful products. The timely return of information on the deficiencies of a polymer system serve to guide polymer programs so that interesting polymer systems will not be overlooked and effort will not be wasted on those of no promise. The need for improved elastomers, the high cost of research, and the large number of polymer systems demands that characterization be conducted on a micro scale in a thorough fashion.

Elastomeric polymers are rarely used as engineering materials, perhaps because in a strict sense they are liquids. Characterization of an elastomer requires that the thermoplastic polymer be transformed into a vulcanized material. Initial solvent and chemical resistance of vulcanized materials are often indicated by the resistance of the basic polymer, but for the more meaningful data and the host of other properties a vulcanizate is required. The characterization of a new polymer is not always straight forward. Generally, the problems can be grouped into four categories: physical nature of the polymer, reactivity toward cross-linking agents, compatibility with reinforcing fillers, and the need for stabilizers and inhibitors (figure 8).

The first problem area concerns the physical nature of the raw polymer. The most desirable form is a soft thermoplastic gum because conventional equipment and procedures have been established for this form. However, many of the newer elastomers may resemble Teflon at room temperature and possess an elastomeric range above 300° or 400°F. These materials cannot be expected to process on conventional equipment. One approach to this high temperature processing problem involves a high temperature internal mixer with provisions for introducing an inert atmosphere. Figure 9 shows a Brabender Plastograph which can mix at temperatures up to 600°F under an inert gas such as nitrogen. High temperature mixing under inert gases would provide a means of

dispersing fillers and other non-reactive ingredients, but would most likely cause cross-linking agents to react during the mixing procedure. Another approach may be the copulverizing of the hard polymer at cryogenic temperatures with compounding ingredients followed by molding of the resultant powder in compression molds.

Compounding difficulties experienced with new polymers are typified by the perfluoroamidine elastomers. At present, these exist as solid prepolymers. When heated, the solid becomes a liquid of low viscosity, evolves ammonia, and becomes a cross-linked elastomer. One approach is to stop the condensation reaction at a viscous processible gum stage where other compounding ingredients can be dispersed into the polymer in a conventional manner.

Many of these features could be termed deficiencies in the polymer system and a recommendation returned to the polymer chemist for a more conventional physical nature of the polymer. However, poor processing features may be characteristic of the new polymer systems. If of sufficient interest new handling techniques for these materials must be developed.

The second problem is vulcanization of the new polymers. A thorough knowledge of the chemical nature is required before a successful system of cross-linking can be devised. Very often the heat and chemical resistant polymers are also resistant to the chemical action of vulcanization. High energy radiation is often used as a research tool to obtain a vulcanizate without resorting to an exotic chemical system.

Characterization studies are often halted for lack of a good vulcanization system. A good example is the promising elastomeric polymer shown in figure 10. The completely fluorinated copolymer of ethylene and propylene is so chemically resistant that chemical cross-linking systems are not known. Often times this deficiency is relayed back to the polymer chemist and a more reactive monomer is substituted. For example a very similar polymer is shown in figure 11. The tetrafluoroethylene is here replaced with vinylidene fluoride and vulcanization with a diamine and metal oxide system is very rapid. A thought comes to mind - why not place only enough vinylidene fluoride in the polymer for cross-linking and retain the completely fluorinated system with its chemical and heat stability? Unfortunately, the amount of vinylidene fluoride must be in excess of that required for a cross-linked network, otherwise the complete network cannot be formed.

A novel approach to vulcanization is possible with the perfluoroamidine elastomer system. As shown in figure 12, the prepolymer contains amine and imine structures which upon heating to 500-600°F liberate ammonia and condense to a stable triazine structure. If polymerization conditions could be sufficiently controlled so that a polymer with terminal condensable structures could be formed, then the system would cross-link without the addition of an excess of cross-linking sites. This approach would also eliminate the possibility of lowering the heat and chemical resistance of an elastomer by incorporating a less stable cross-linking agent in the network.

The third difficulty, that of a reinforcing filler for new polymers is at present an unsolved one. Carbon black in its many forms leaves much to be desired - especially for the fluorinated polymer systems. Silica fillers were found useful in silicone elastomers but have deficiencies when used with the newer materials. New approaches are needed in this area to obtain optimum mechanical properties with these newer polymers.

The last area involves stabilizers and inhibitors for high temperature elastomers. Naturally, the attempt is to prepare polymers which do not require stabilizers or inhibitors, but to date very few have been made. Polymeric materials are complex and often the idealized structure does not exist. Physical and chemical flaws in the polymer chains are possible weak links. The problem is further complicated with the need for inhibitor action at temperatures which usually degrade even the inhibitor. A study of the inhibiting action of inorganic structures against oxygen may provide leads for these additives. Other inhibitors for chemical attack, catalytic effects, ultraviolet and nuclear radiation, etc., are needed.

In summary, I want to emphasize the importance of timely characterization of new polymer materials. The new polymers, tailor made for the extreme environments encountered in Air Force systems, may be unconventional materials and most likely will require new processing techniques, unheard of vulcanization systems, new reinforcing fillers specially suited to specific polymer systems, and inhibitors capable of 600-1000°F operation. I hope this brief discussion will give an appreciation of the magnitude of the research problems involved in the characterization of new elastomeric polymers.

Engineering

The Elastomers Section of the Directorate of Materials and Processes conducts research for materials which are broader in scope than those described by the term "elastomeric". Many of the materials are better described by such adjectives as compliant, resilient, or flexible. The scope of materials will become evident in the subsequent discussion of this phase.

Certainly one of the major areas of our research concerns materials for use as seals. Current programs are seeking seal materials for anticipated service over a temperature span of about 2500°F and in environments which range from innocuous to that of fluorine gas. The inherent simplicity of elastomeric, or resilient seals is of unquestioned desirability. During initial discussions of sealing problems for systems operating at environmental extremes, these problems are often dismissed with comments such as: "We'll use metal O-rings," "Weld it shut," or "A metal bellows will take up dimensional changes there". Not always, but frequently an opportunity exists to meet the authors of these phrases again at a later date as they inquire of materials suitable for a simple seal, such as an elastomeric O-ring.

In designing elastomeric seals for cryogenic applications, most polymer people are aware as soon as an elastomer is below its glass transition temperature, it is not elastomeric and, hence, cannot effect a seal by overcoming dimensional changes of other members. It is fortunate that not all people are aware of this view. In figure 13, the successful design of a cryogenic seal utilizing elastomeric O-rings is illustrated as currently planned for use on the Centaur. It differs from conventional O-ring seal designs in that no groove is present and a much higher compression of the O-ring is employed. Seals based on fluorinated elastomers, Hypalon, neoprene, and natural rubber have been successfully evaluated at temperatures about 300°F below the glass transition range. It should be emphasized that high compression does not produce effective seals with all types of vulcanizates. Current investigations are directed to elucidation of the effects of polymer structure upon performance as cryogenic seals.

For very high temperatures, composite seals utilizing a resilient inorganic fiber skeleton filled with a compliant sealing material have exceptional promise. In a crude analogy, a seal for cold water might consist of a resilient pad of steel wool impregnated with grease. Figure 14 illustrates the performance of a seal based on this concept at rather rigorous conditions. No other types of seals investigated approached this level of performance. The last item of data in figure 14, however, indicates a problem area for this type of seal. The very high compressive forces required to effect the seal preclude use of this concept for low pressure sealing, as for cabin pressurization. At low levels of strain, the corresponding levels of stress are tens of thousands of times those required for elastomeric vulcanizates.

Sealants for both unmanned and manned aerospace vehicles cover an extremely broad area. Sealants are an integral part of the engineering projected for large aerospace vehicles to be launched from the earth's surface. Certainly materials resistant to degradation by the combined aerospace environment of vacuum, temperature, and u.v. radiation are required. The assembly of vehicles above the earth's surface will also require sealants, although the problems become much more complicated. Conventional techniques for sealant application such as refrigeration, mixing immediately prior to use, and carefully controlled curing conditions appear impractical, at best. The activation of sealants by depressurization and by shear is currently being investigated. Perhaps one of the most intriguing problems associated with sealants is the design of a system which will remotely seal the punctures of aerospace vehicles. This area of research is made difficult by the nebulous data available on the frequency and magnitude of punctures which are to be expected. Even if precise data of this type were available, it would appear to be of little comfort to the occupant of a punctured vehicle unless he could use the resultant report to plug up the hole and preserve his vehicle's internal environment.

One concept currently being considered to provide this self-sealing capability is shown in figure 15. Inter-layers of a separated polymeric material and a very active cross-linking agent, which are stable when uncombined, are activated by the mixing occurring on puncture. Silicone and polyurethane polymers which will flow on puncture and will gel on contact with catalytic agents are promising. The major problem of this concept, other than the ever present one of high reliability, is associated with the necessity of a low weight penalty. Apparatus simulating the puncture of aerospace vehicles has been designed and utilized for the evaluation of self-sealing concepts and systems. This apparatus is shown in figure 16; it consists essentially of three connected chambers, the first two of which are evacuated. The third chamber is maintained at atmospheric pressure and is sealed from the second evacuated chamber by the test specimen. By closing a solenoid valve after passage of a 22 caliber bullet fired from a rifle in the first chamber into the central evacuated chamber, a comparatively high vacuum can be maintained on the portion of the test specimen simulating the outer portion of the aerospace vehicle after puncture.

The compactness and light weight of expandable structures appear attractive for both manned and unmanned vehicles. The further capability of rigidization after expansion of these structures makes this concept even more attractive. While a variety of systems currently under investigation are designed to attain rigidization after expansion of the structure to the desired shape, many of these systems would result in only a low degree of rigidization. Rigidity of this type is designed to resist the minor forces resulting from light pressure and the pressure of rarefied atmosphere, and is largely tailored to the demands of satellites comprising parts of communications systems. Some Air Force programs have been largely directed toward obtaining rigidity in a truly structural sense. The general principle is illustrated in figure 17. The flexible, and hence expandable, structure consists of three layers. The outer layer is a fabric externally coated with an

elastomeric coating. The middle layer consists of a fiberglass or similar reinforcing fabric impregnated with a viscous prepolymer. The inner layer is a light weight barrier to prevent adhesion during storage with the structure in a compacted state. Expansion is attained by the release of an inflating gas. All or part of the inflating gas may consist of a reactant which converts the liquid prepolymer to a rigid mass which is reinforced by the fibrous material. Typical gaseous reactants are amines and water vapor. Some estimate of the degree of rigidization obtained in the laboratory can be gained from figure 18 which illustrates such a system described before and after rigidization. Improvements in this concept, or new concepts, are required to improve the temperature capability of the system and to minimize the weight penalty incurred. Silicone and other resin systems may be of promise.

Efforts to develop elastomeric vulcanizates for resistance to elevated temperatures fall essentially into two categories which are exclusive of seals and sealants. The first of these categories embraces vulcanizates which must maintain a substantial degree of strength at elevated temperatures. Projected applications for this class of elastomers would include tires and devices for acoustic and vibrational damping. In these areas the problem is further complicated by the necessity of thermally stable bonding of the vulcanizates to fibrous or metallic substrates. In areas requiring elastomers of high resilience, new hydrocarbon elastomers have shown promise. Figure 19 illustrates a comparison of strengths of vulcanizates, including a natural rubber vulcanizate which is typical of the types used in tire fabrication. Again much higher temperature capability is desired.

The second area of high temperature applications of elastomers involves temperatures which increase by an order of magnitude. Temperatures involved range up to 6500°F, and applications include solid propellant rocket insulation, external rocket insulation, and re-entry drag devices. Problems of adhesion are apparent in all these areas. Certainly criteria of capability of various elastomeric systems over this very broad temperature span is required. Inflated drag devices would additionally require a low permeability to the inflating gas and a higher degree of structural integrity at temperature.

Seals for liquid propellant systems remain a critical problem area. Increases in the energy output of propellant systems have invariably been attended by increases in the chemical activity of the fuels and oxidizers toward seal materials. Further complications arise from the shock sensitivity of seals containing absorbed oxidizers. Yet the simplicity and low weight penalty of elastomeric seals is highly desirable. Particularly difficult seal problems are encountered with chlorine trifluoride, fluorine, and nitrogen tetroxide.

In conclusion, the necessity of close liaison between the applied research programs and the fundamental research areas should be re-emphasized. Guidance is often operative in both directions. Finally, the magnitude of the problems in the area of elastomer research dictates the cooperation of Government, industry, and academic personnel in obtaining solutions.

BIBLIOGRAPHY

1. Montermoso, J.C., "Proceedings Sixth Joint Army, Navy, Air Force Conference on Elastomer Research and Development," 18-20 October 1960.
2. Brown, H.C., "Synthesis of Semi-Organic Fluorine Containing Polymers," WADD TR 59-272, Parts I and II, May 1959 and June 1960.
3. Bartholomew, E.R., Eykamp, G.R., and Gibbs, W.E., "High Temperature Elastomeric Compounds and Polymers," Rubber Chem. and Tech., 32, 1587, 1959.
4. Schwarz, E.G., "The Micro Compounding and Evaluation of Rubber-like Polymers," WADC TR 57-247, July 1957.
5. Spain, R.G., et al, "Research and Development on High Temperature Fuel Resistant Rubber Compounds," WADC TR 55-492, Parts III-VI, 1958-1961.
6. Paciorek, K.L., et al, "Mechanism of Cross-Linking in the Vulcanization of New Elastomeric Polymers," WADC TR 59-129, Parts I and II, July 1959 and July 1960.
7. Jackson, W.W., "Vulcanization of Rubber With High Intensity Gamma Radiation," WADC TR 55-57, April 1955.
8. Smith, F.M., "Development of High-Temperature Resistant Rubber Compounds," WADC TR 56-331, December 1956.
9. Hayes, R.A., "Research on High-Temperature Resistant Rubber Compounds," WADC TR 56-331, Parts II, III, and IV, February 1958, April 1959, April 1960.
10. Kitchen, L.J., et al, "High Temperature Resistant Elastomer Compounds," WADC TR 56-331, February 1961.
11. Sabanas, M., "Composite Inorganic Resilient Seal Materials," WADC TR 59-338, Parts I and II, Oct. 1959, and April 1960.
12. Weitzel, D.H., Robbins, R.F., "Elastomeric Seals and Materials at Cryogenic Temperatures," 1st Quarterly Progress Report, Contract AF 33(616)-61-04, March 1961.

TABLE I

Temperature	Wavelength below which 98% of the energy emitted by a blackbody will fall	Relative Energy
500° F	32 μ	1
1000° F	21 μ	~ 5
2000° F	13 μ	~ 43
4000° F	7 μ	~ 470
10000° F	3 μ	~ 14000

APPLICATIONS OF ELASTOMERS IN AEROSPACE VEHICLES

- Shock & Vibration Mounts
- Flexible Connectors
- Erosion Resistant Coatings
- Thermal Installation
- Radiation Shielding
- Adhesives & Tapes
- Solid Propellants
- Fuel Containers
- Cushioning
- Fluid Seals
- Tires
- Reentry Deceleration Devices
- Rocket Motor Insulation
- Structure Seals & Sealants
- Meteorite Self Structure
- Electrical & Electronic
- Expandable Structure

Figure 1.

AEROSPACE ENVIRONMENTS

● Pressure, 10^{-11} mm Hg to 10,000 psi.

● Temperature, -400° to 6000° F

● Radiation, Solar, Nuclear, Cosmic

● Shock and Vibration

Figure 2.

PREVIOUS WORK

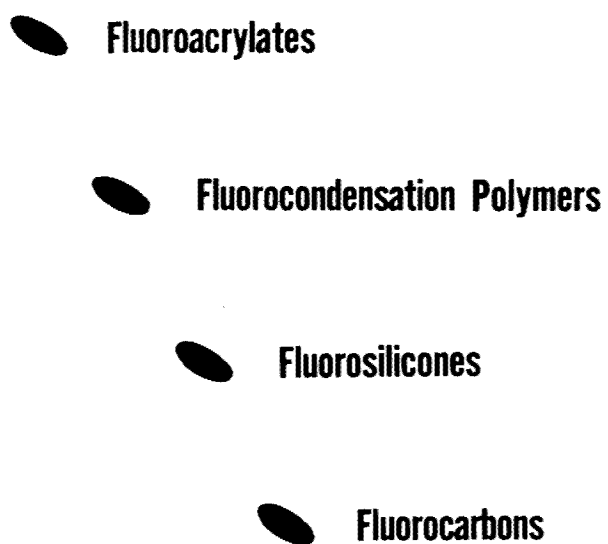
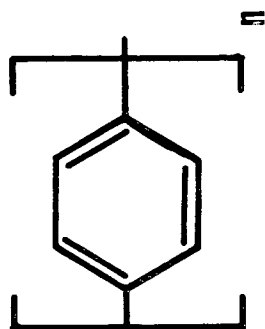
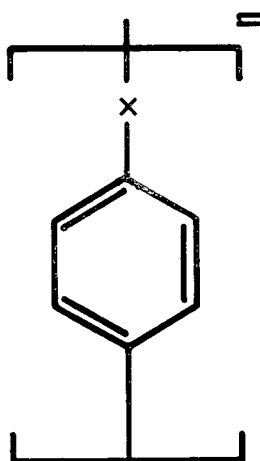
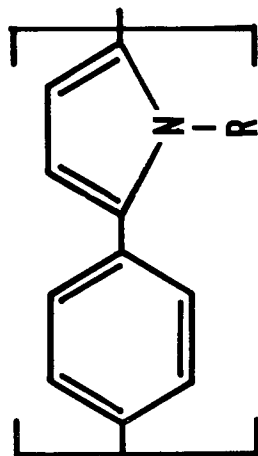
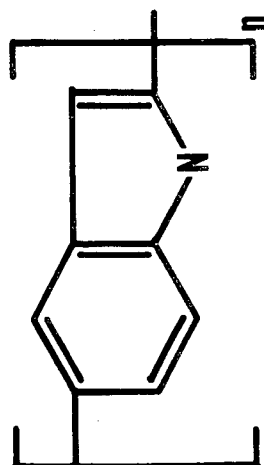


Figure 3.

POLYAROMATICS



POLYHETEROCYCLICS



LADDER POLYMERS

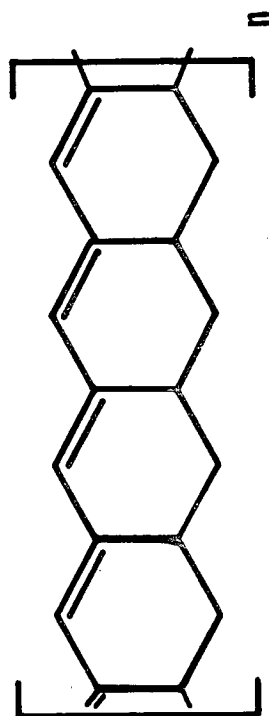


Figure 4.

PERFLUOROAMIDINE POLYMERIZATION

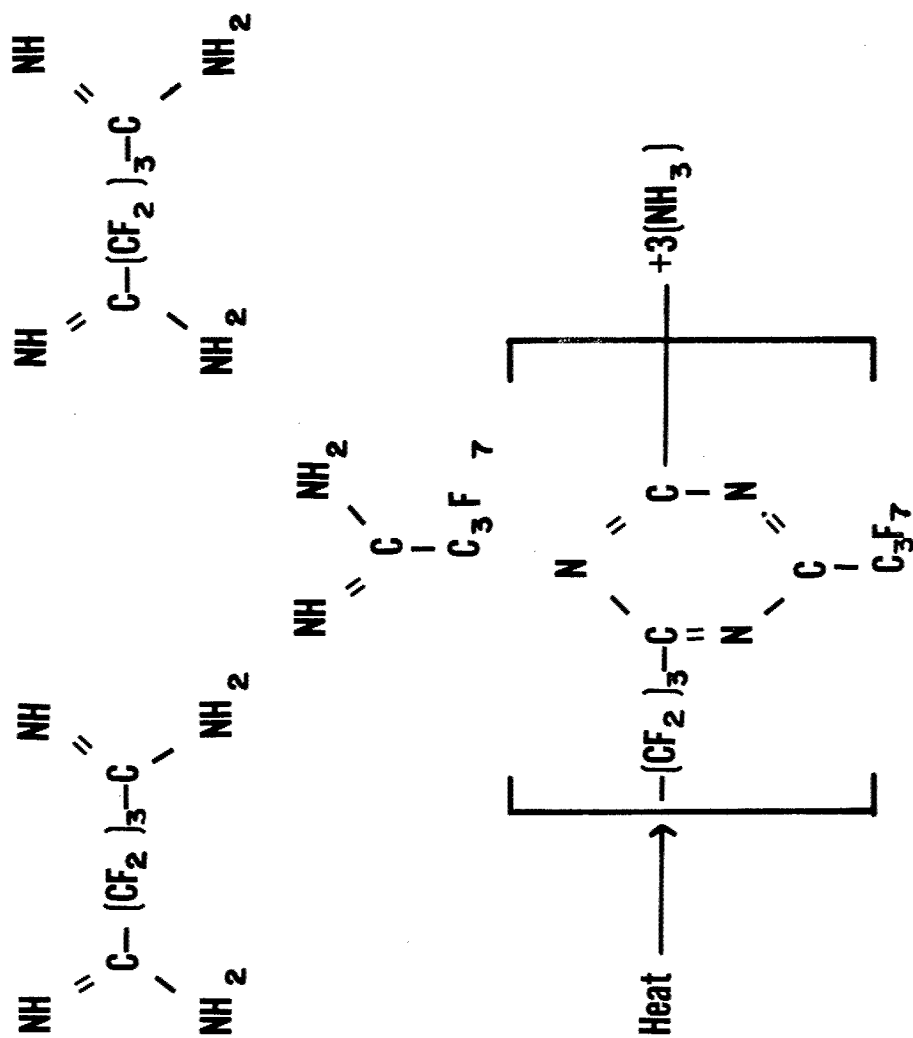


Figure 5.

LOW TEMPERATURE POLYMERIZATION

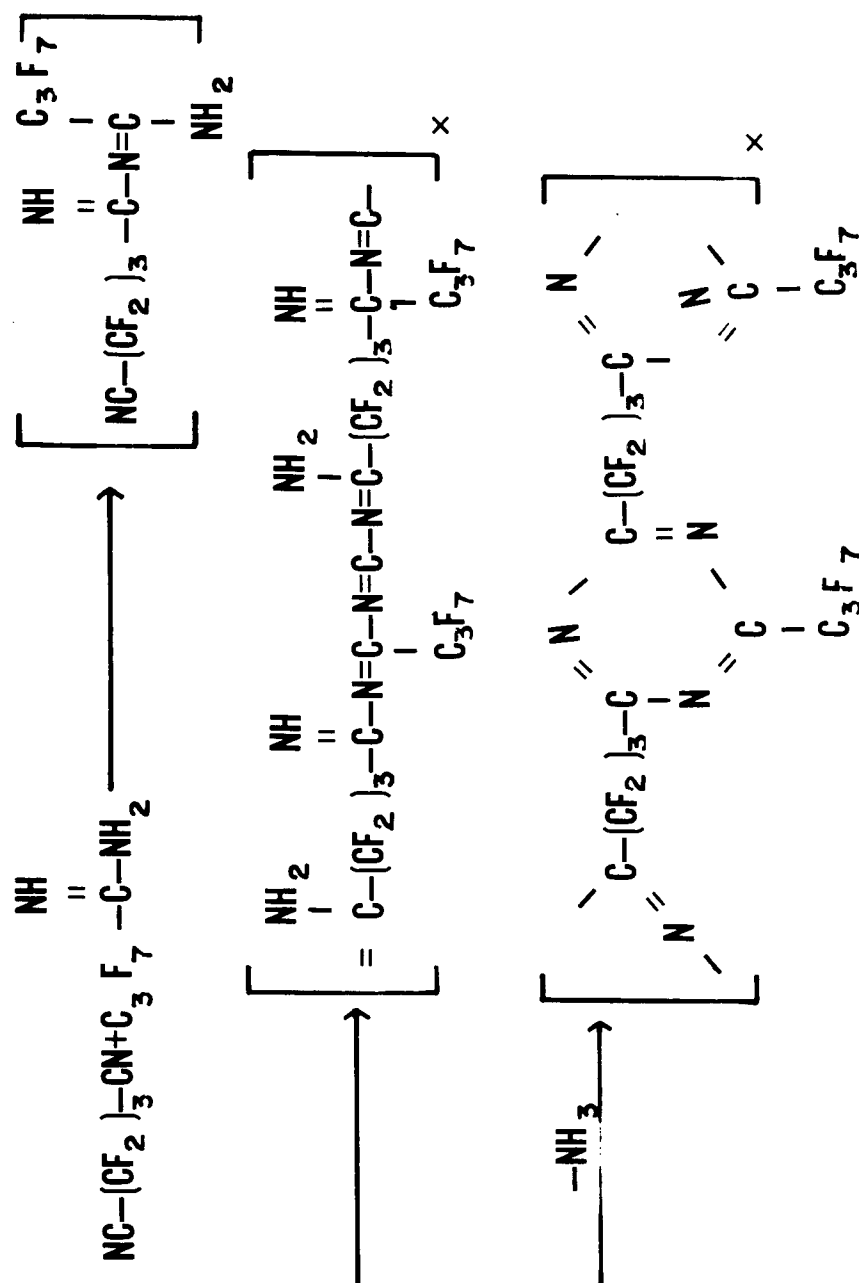


Figure 6.

POLYBENZIMIDAZOLE SYNTHESIS

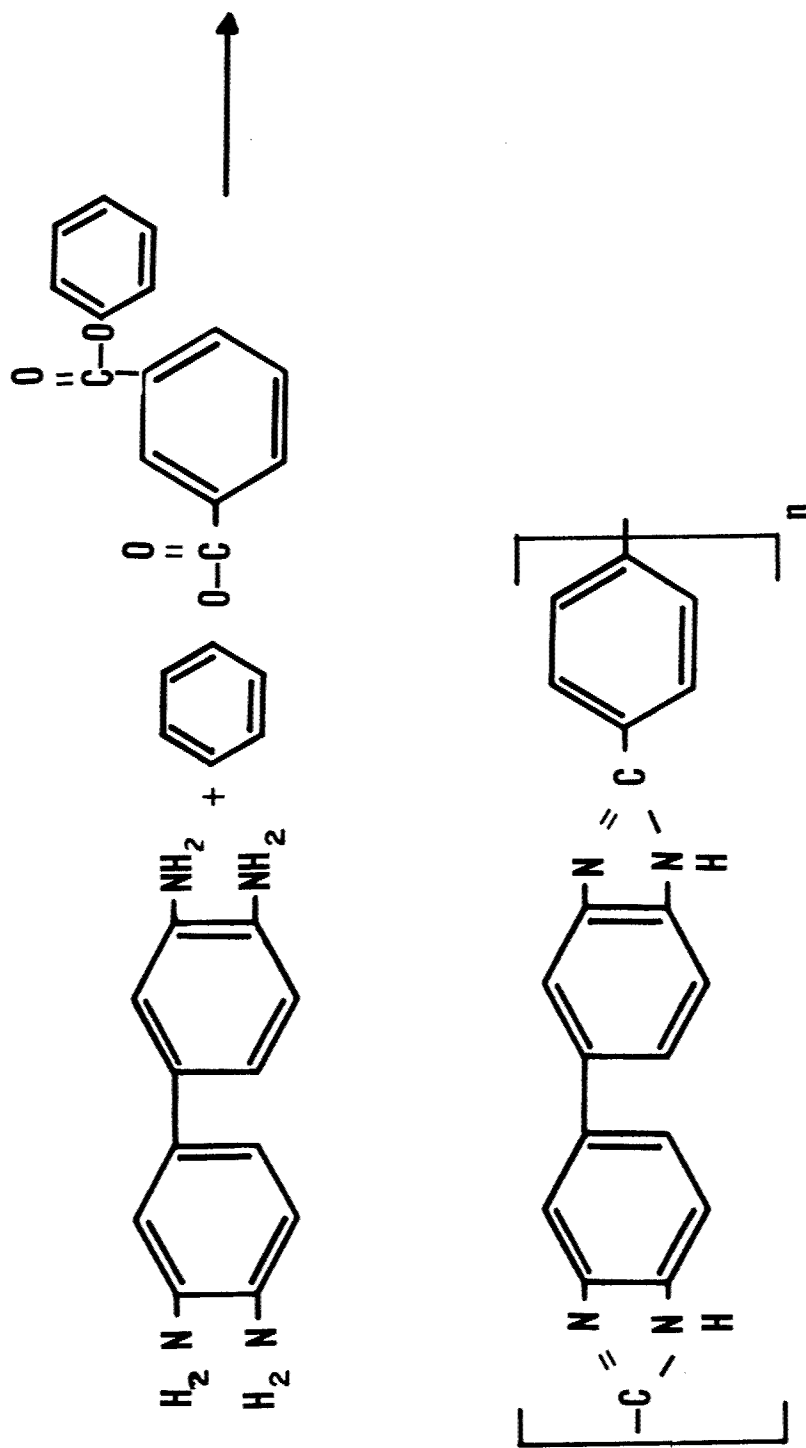


Figure 7.

POLYMER CHARACTERIZATION

- **Physical Nature Of The Polymer**
- **Reactivity Toward Cross-Linking Agents**
- **Compatibility With Reinforcing Fillers**
- **Need For Stabilizers And Inhibitors**

Figure 8.

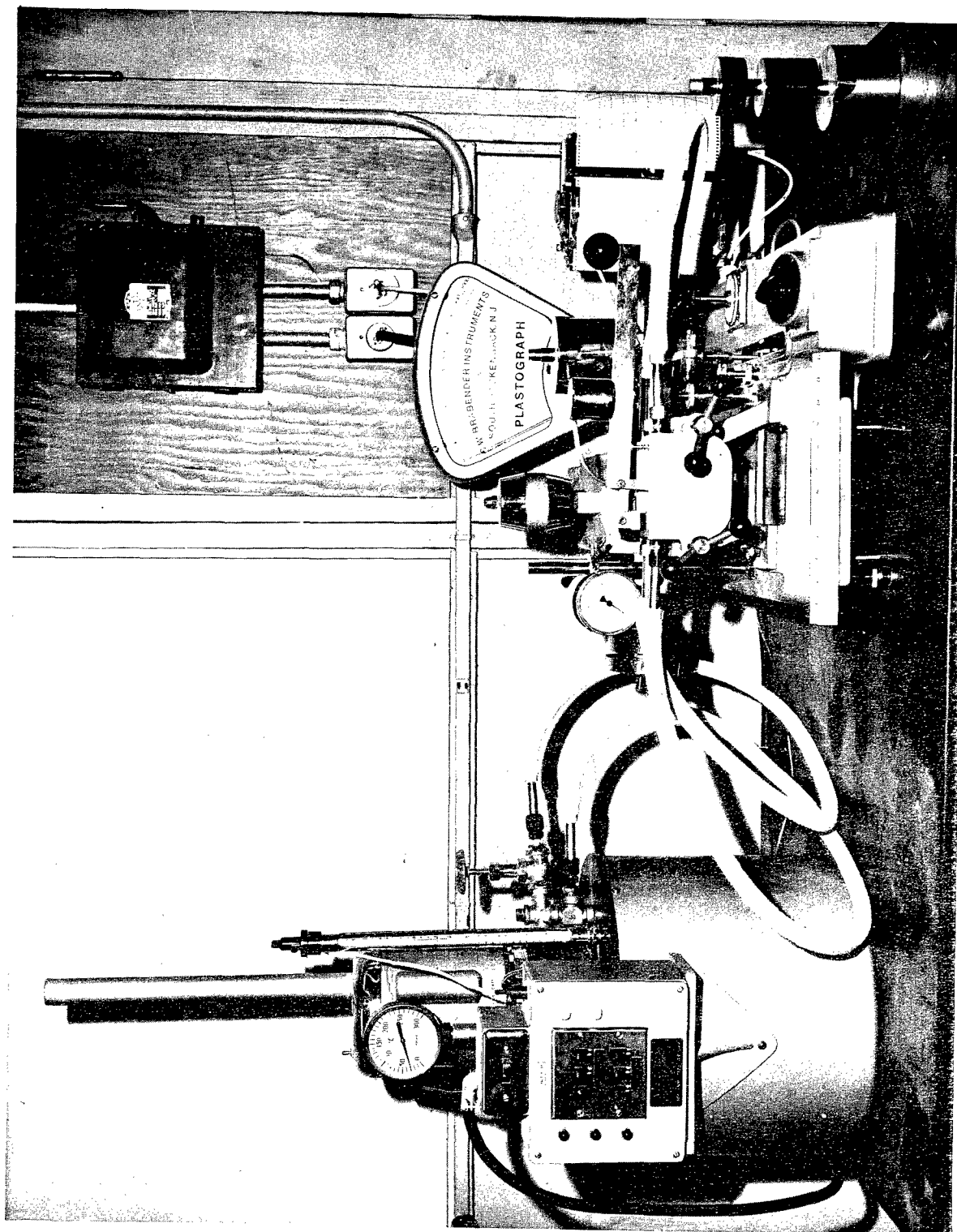


Figure 9.

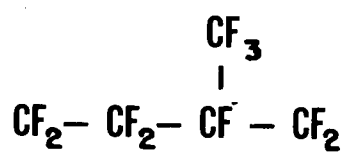


Figure 10.

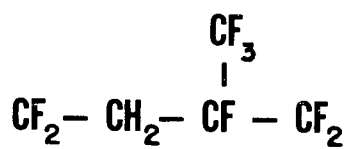


Figure 11.

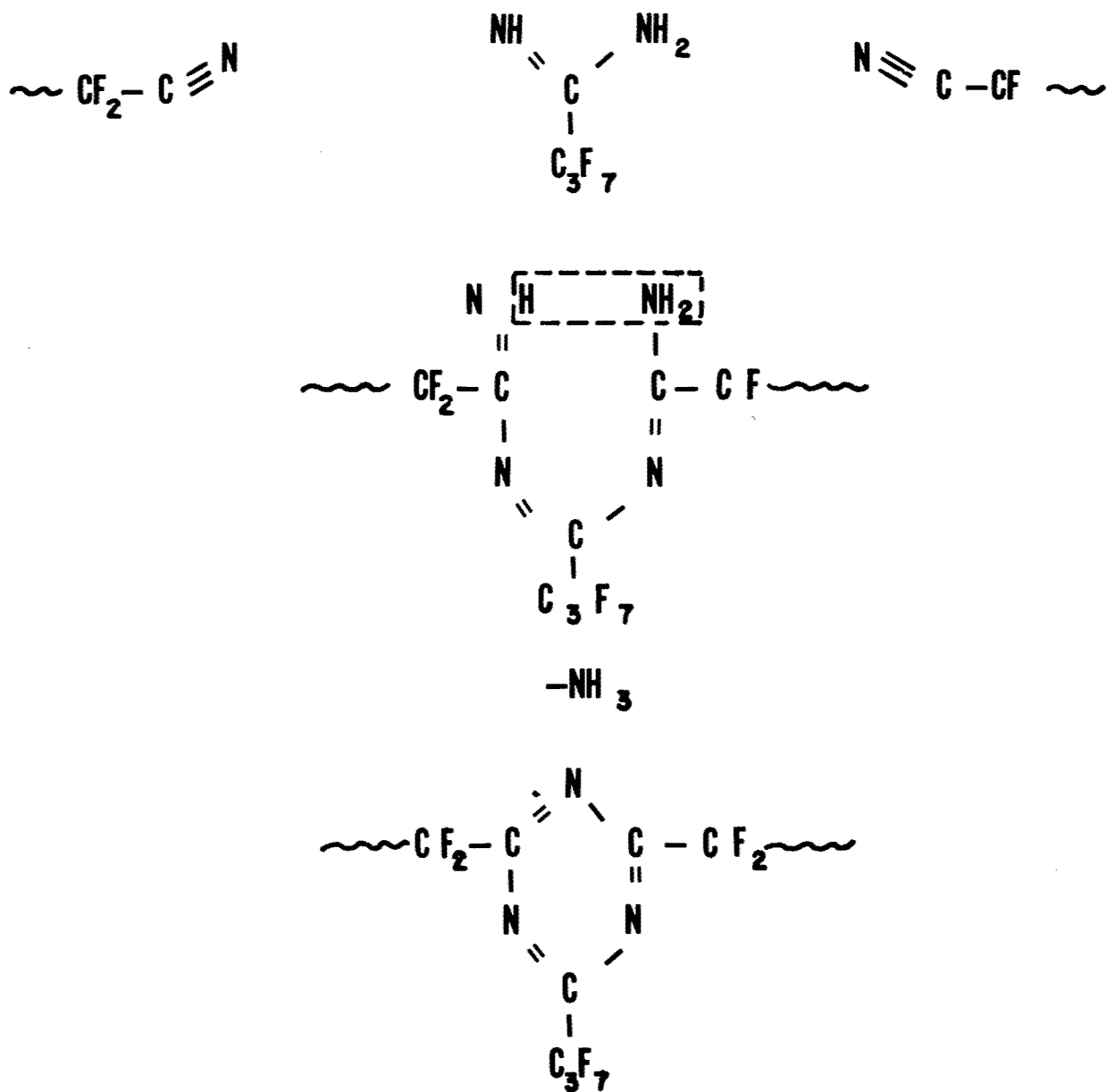


Figure 12.

STATIC O-RING SEALS

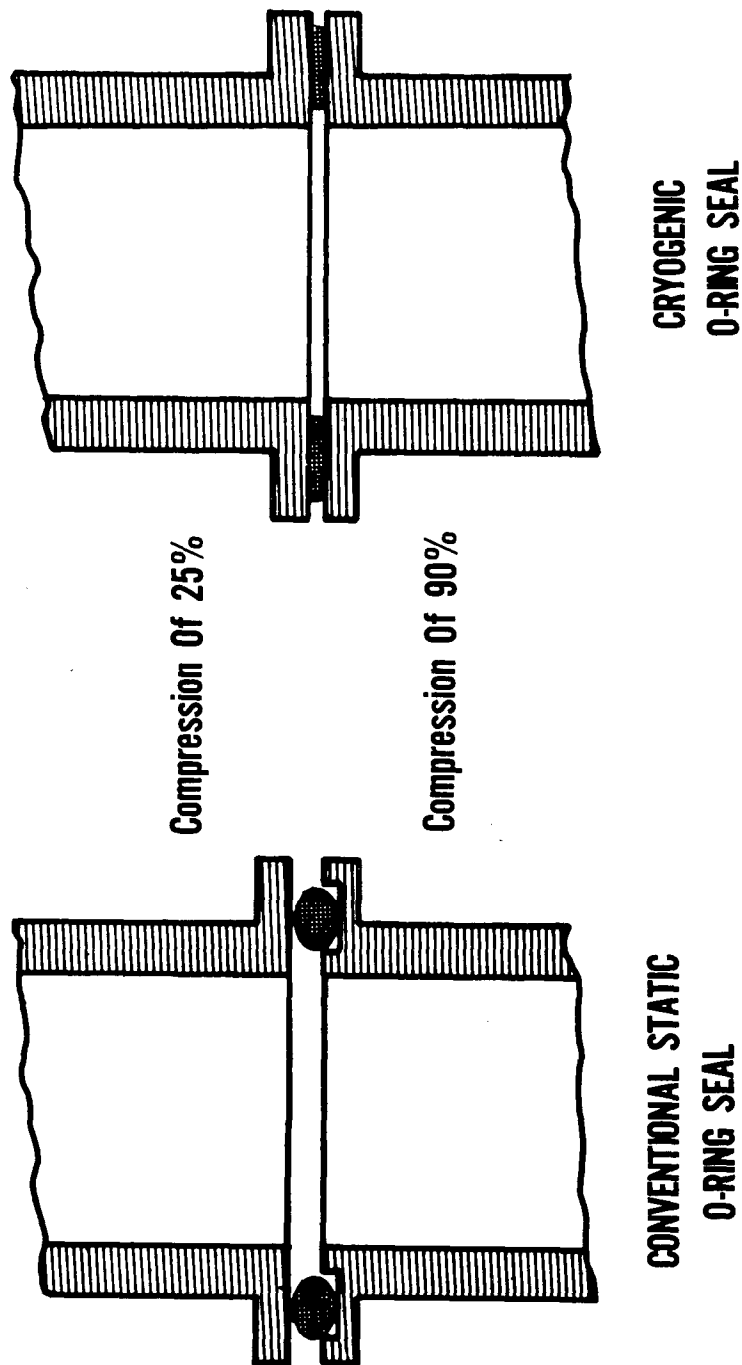


Figure 13.

METALLIC COMPOSITES AS A ROD SEAL

Type Of Seal	Wedge
Diameter Of Rod	0.5"
Temperature Cycle	80°F To 1000°F
Pressure	4000 PSI
Cycles To Failure	114,000 Dynamic, 6 Thermal
Force To Effect Initial Seal	350 Lbs.

Figure 14.

SELF SEALANT CONCEPT

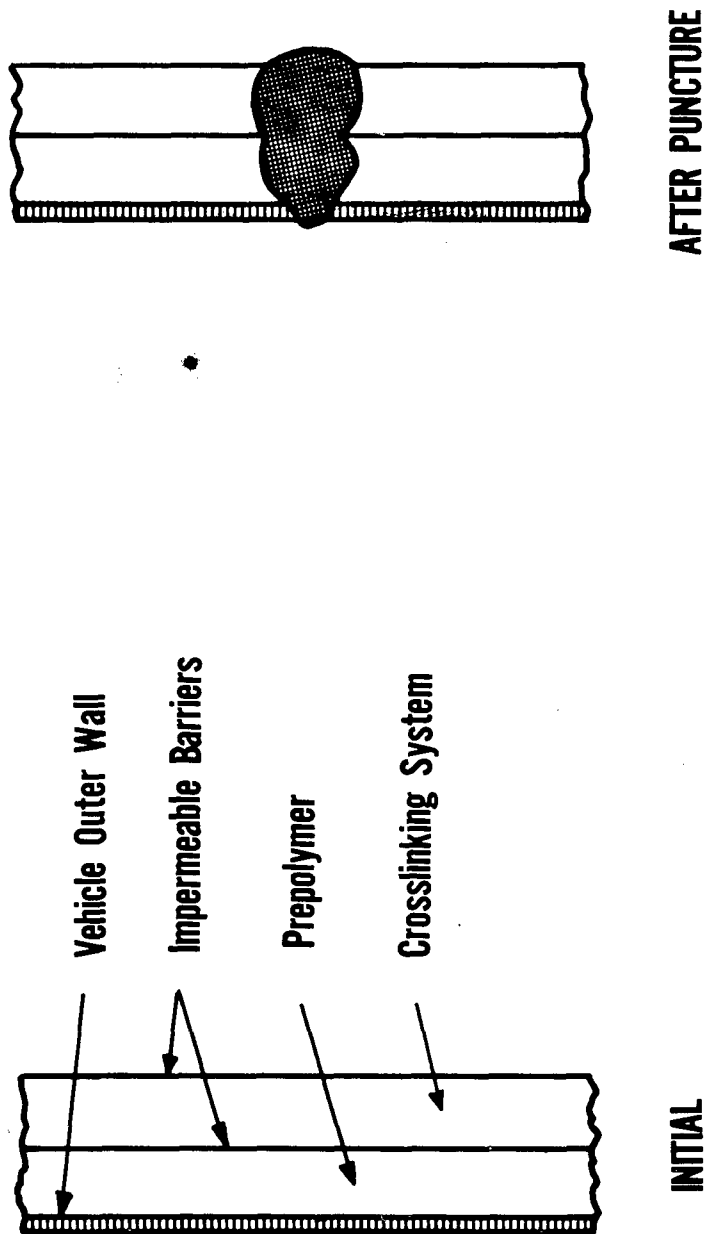


Figure 15.

VEHICLE PUNCTURE SIMULATOR

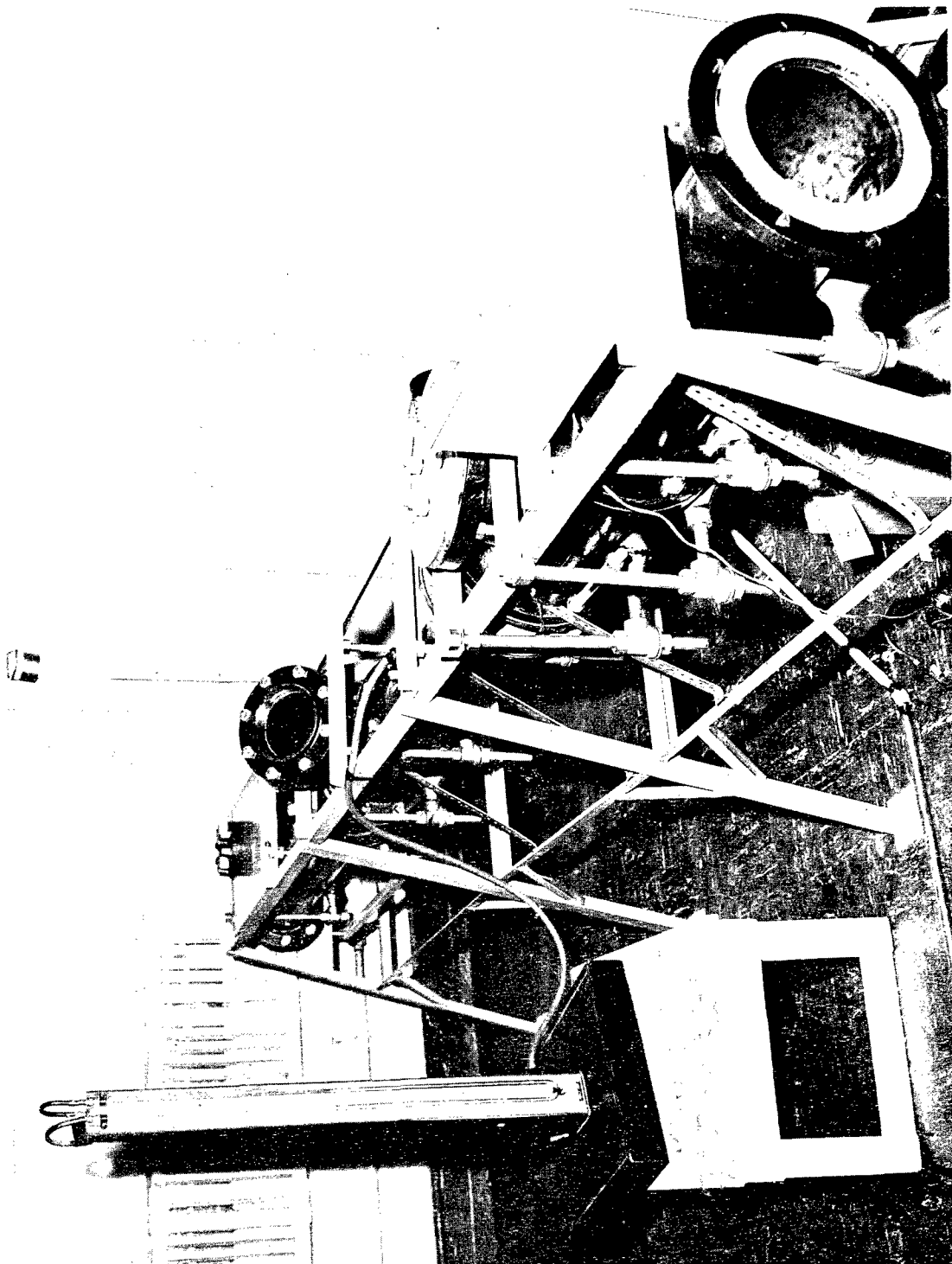


Figure 16.

RIGIDIZATION CONCEPT

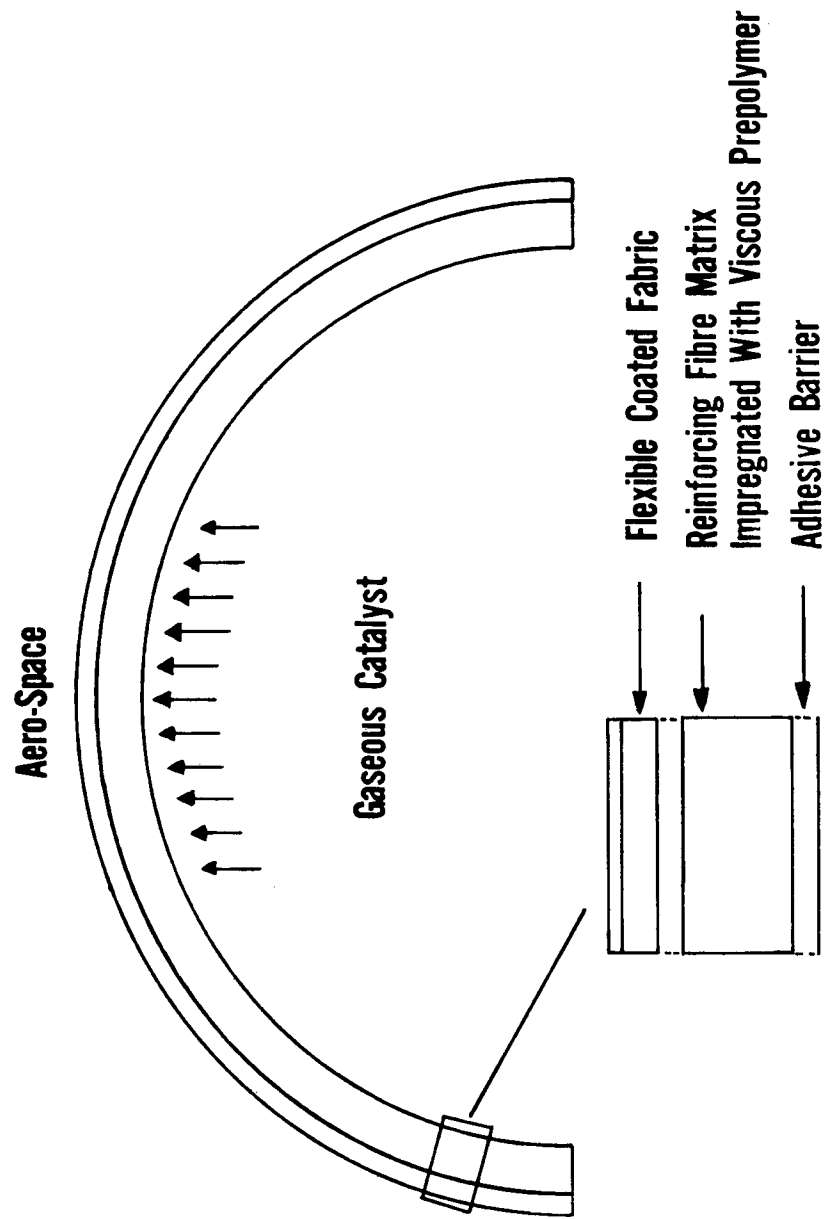


Figure 17.

EXPANDABLE-RIGIDIZABLE STRUCTURE

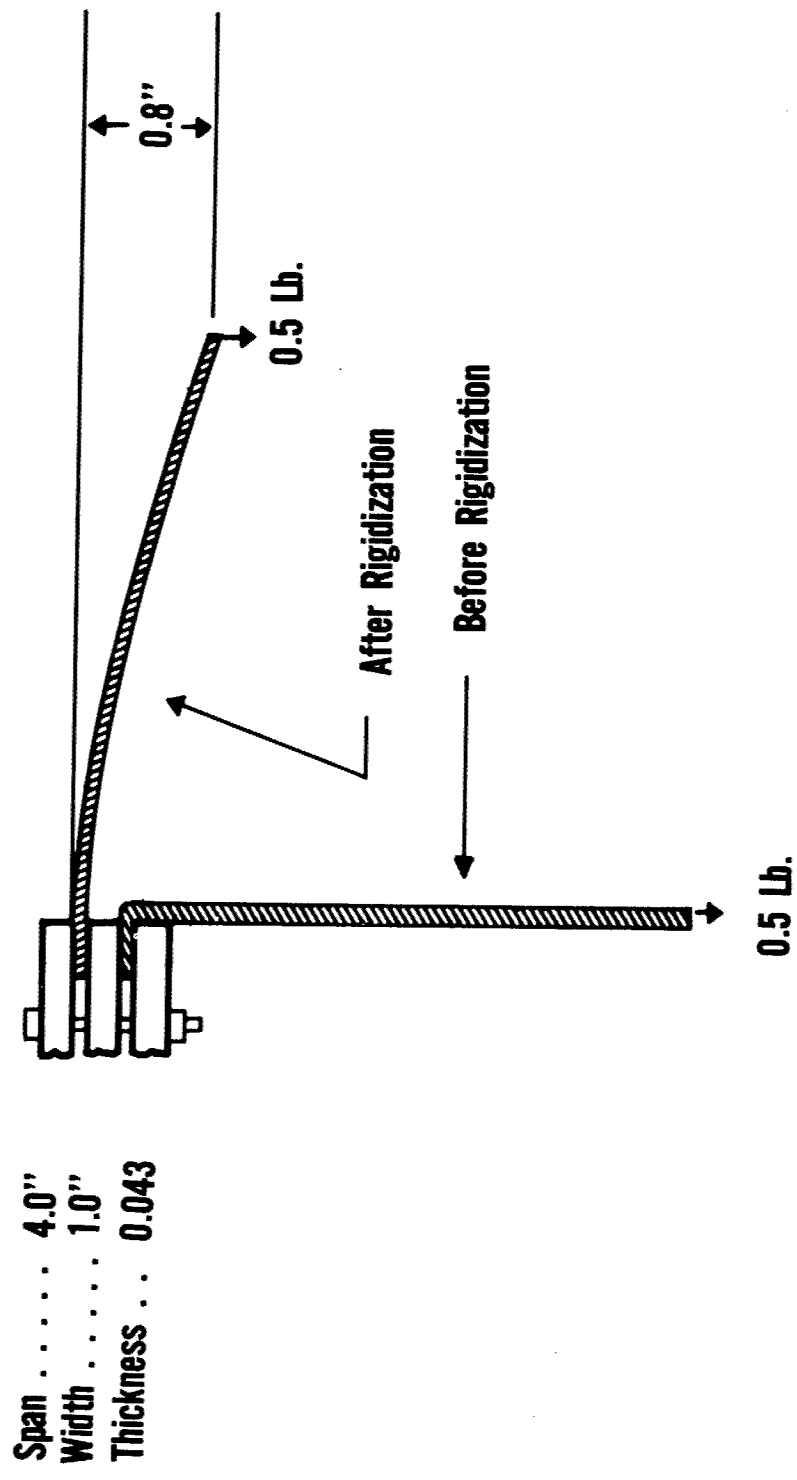


Figure 18.

TENSILE STRENGTHS OF VULCANIZATES

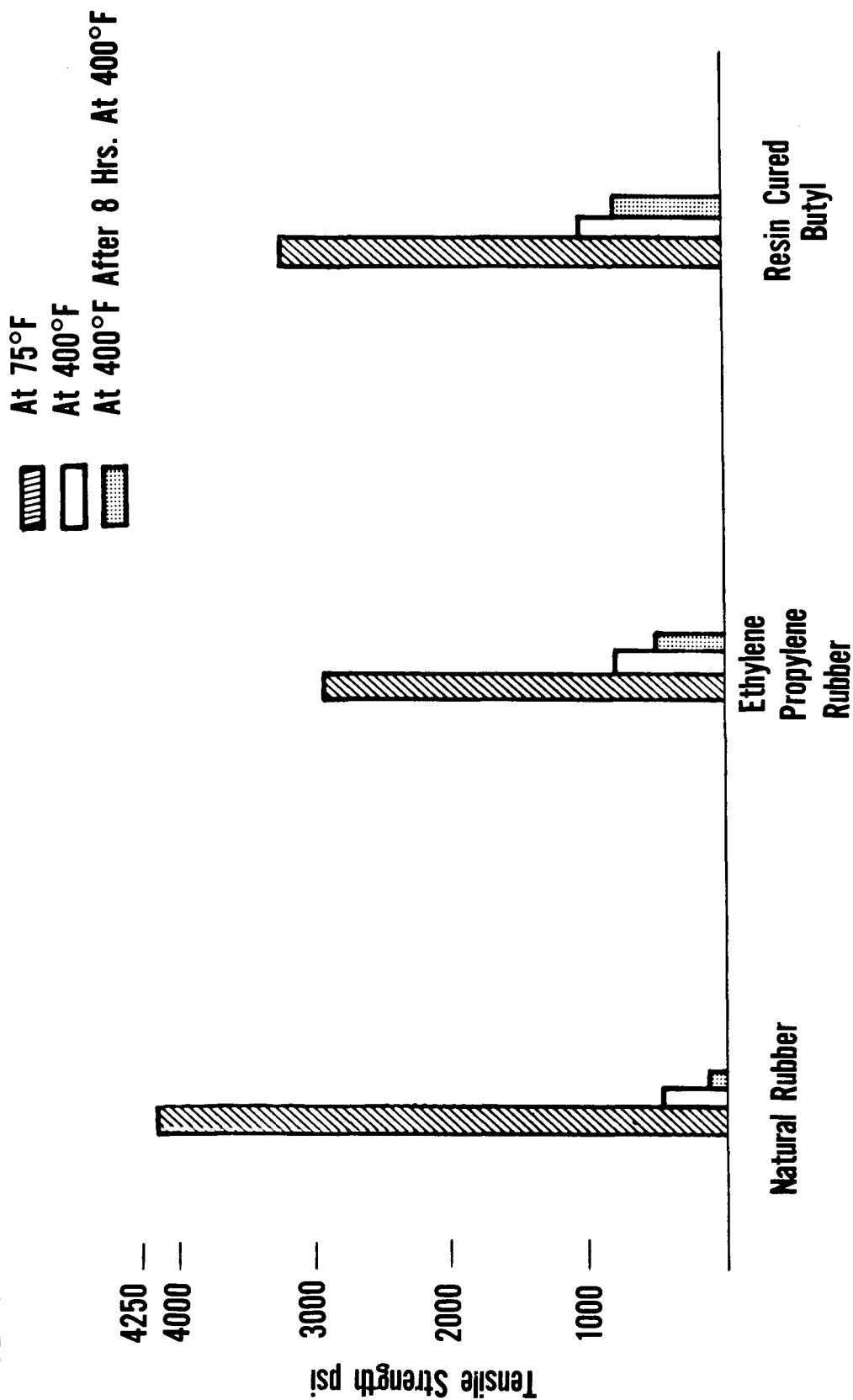


Figure 19.

COATINGS

Chairman

Mr. R. M. Van Vliet

Speaker

Mr. R. A. Winn

Lt J. J. Mattice

Mr. J. H. Weaver

Mr. H. Marcus

Lt. L. N. Hjelm

Panel Member

Mr. J. Wittebort

THERMAL EMITTANCE MEASUREMENTS

R. A. Winn

Directorate of Materials and Processes, ASD

With the advent of satellites, space vehicles, and space probes, our attention is directed toward thermal protection of structures in a somewhat new environment. The term "spacecraft" will be used in this paper to include satellites, manned or unmanned space vehicles and space probes. With these spacecraft in an environment of ambient pressures less than 10^{-8} mm of mercury, heat transfer to and from the craft will be limited to radiative modes. With this limitation the emittance, reflectance, and absorptance of materials are the important factors determining the ultimate heat rejection or heat acceptance ability of the exterior surfaces of a spacecraft.

Of equal importance is the problem of thermal protection of these vehicles upon re-entry into the earth's atmosphere. Because of the severe frictional heating encountered during re-entry by a vehicle, such as the Dyna-Soar, an efficient radiating skin surface is most important for keeping vehicle temperature within safe limits.

For the more common materials there is a wealth of information, including emittance values. Unfortunately, there are many instances where there are wide discrepancies between data from different investigators, presumably, for the same materials. In the case of emittance measurements, there are cases when it was not specified whether the measurement was total normal emittance or total hemispherical emittance. Surface conditions are factors that require more than just casual attention.

There is a dearth of information for the newer materials. The Air Force is interested in this type of information for a variety of materials; in order to provide this much needed information, this Directorate has initiated several programs with commercial research laboratories and universities. In some cases, these programs are for the generation of data for materials of interest; in other cases, the emphasis is on the development of improved techniques of measurements or for the extension of temperature capabilities. Therefore, most measurements are made on a spectral basis using suitable integrating techniques to derive the total normal emittance or spectral normal emittance data needed by the vehicle designers. Total hemispherical emittance measurement techniques often use the method of heating a sample by its own electrical resistance (Joulian heating), measuring the power input and specimen temperature, then calculating the total hemispherical emittance. Such techniques do not lend themselves readily for nonelectrically conducting materials. Measurements of total normal emittance seem to be somewhat simpler to make and the equipment can be used for electrical conductors as well as for electrical insulating materials.

Although there has been some laxity in the past about distinguishing between emittance and emissivity, Prof. A. C. Worthing has emphasized (1) the distinction, and investigators have been more concerned recently with properly identifying the properties they have been measuring. Worthing states, "That in accord with the usage that an 'ivity' ending shall denote a characteristic of a material, the term 'emissivity' is limited to a comparison with a blackbody under conditions where the individual characteristics of bodies composed of the material under consideration are eliminated. Since the radiation characteristics of a body depend in part upon its opaqueness and the roughness of its surface, these factors must be considered in forming an acceptable definition of emissivity.

Accordingly, the emissivity of a material is defined as the ratio of a rate of emission of radiant energy by an opaque body with a polished surface composed of that material as a consequence of its temperature only, to the corresponding rate for a blackbody at the same temperature."

"In accord with the usage that an 'ance' ending shall denote a characteristic of a body or a portion of a body rather than of the material composing it, an emittance for a body at some constant temperature is defined as the ratio of the rate of emission of radiant energy by the body in consequence of its temperature only to the corresponding rate for a blackbody at the same temperature."

According to Kirchhoff's law: At a given temperature, the total emissive power for any body is equal to its absorptivity multiplied by the total emissive power of a perfect blackbody at that temperature. This may be expressed as:

$$E = \alpha E_B \quad (1)$$

where E is the emissive power of a material

E_B is the emissive power of a blackbody

α is the absorptivity of a material

This may be written as:

$$\frac{E}{E_B} = \alpha = \epsilon \quad (2)$$

since ϵ , the emissivity is numerically equal to the absorptivity.

Radiation properties usually are defined with respect to a theoretical material or standard that is completely absorbing. Known as a blackbody, it is a perfect radiator in that it will emit the maximum amount of radiation per unit area that is possible to be emitted by a body at that particular temperature. The Stefan-Boltzman Law shows how the total radiant flux from a unit area of a blackbody varies with temperature:

$$W = \sigma T^4 \quad (3)$$

where W is the total radiant flux from a unit surface, σ is the Stefan-Boltzman constant, and T is the absolute temperature. In practice, the true blackbody is never realized and a measure of the success in approaching true blackbody conditions may be the term $\epsilon_{(T_h)}$, the total hemispherical emittance.

A few more definitions are required at this point. The transmittance of a material may be defined as the ratio of the radiation transmitted through the material to the radiation incident upon the material. The absorptance and the reflectance can be defined, likewise, as the ratios of the radiation absorbed by the material and the radiation reflected by the material to the radiation incident upon the material, respectively. The interrelation of absorption, transmission, and reflection of radiant energy is illustrated in figure 1. Figure 1 is for a general case where a transparent material is being irradiated. From this figure and following the concepts of the conservation of energy, it is seen that reflected energy (ρ), transmitted energy (τ) and the absorbed energy (α) may be combined to equal the total incident energy. This may be stated as:

$$\rho + \alpha + \tau = 1 \quad (4)$$

For opaque materials where the transmitted energy is zero, ($\tau = 0$) the reflectance and the absorptance are complementary:

$$\rho + \alpha = 1 \quad (5)$$

Therefore emittance was defined as the ratio of radiation from a particular specimen to the radiation of a blackbody operating at the same temperature; and emissivity is defined as the ratio of the radiation from a material with an optically smooth surface which is thick enough to be opaqued to the radiation from a blackbody.

On this basis, several relations similar to those shown for absorptance, reflectance, and emittance may be written for absorptivity (A), reflectivity (R), and emissivity (E):

$$A + R = 1 \quad (6)$$

$$\text{or} \quad R = 1 - A \quad (7)$$

$$\text{and} \quad A_{t1} = E_{t1} \quad (8)$$

where the subscripts t1 indicate a certain temperature.

Materials at temperatures in excess of absolute zero will radiate energy. The rate of radiation from a blackbody is a function of temperature alone and is proportional to the fourth power of the absolute temperature. The blackbody radiation is the maximum radiation possible from a material at a specific temperature and wavelength; therefore, it is reasonable to compare radiation from all other materials (non-blackbodies) with the radiation from a blackbody at the same temperature for a basis of comparison. The radiation from a non-blackbody depends upon the material, its temperature, and the condition of its surface.

A blackbody will emit or absorb the maximum radiation possible at a specific temperature. Obviously for maximum heat transfer, one would choose a blackbody radiating to another blackbody at a lower temperature. Since a true blackbody is only approached, never realized, it is necessary to know how near to true blackbody conditions a particular material really comes. This indicates that a blackbody (under ideal conditions) should be chosen as a reference or a standard, and all other materials or bodies compared with it determine their radiation properties. This has been borne out by the definitions of several terms with which we are working.

Blackbodies have received close attention with the possibility of constructing cavities that approach very closely to true blackbody conditions. It is not unreasonable to expect the radiation from so-called blackbody cavities to be 0.995 the radiation from a true blackbody. Careful design and precise temperature control have permitted very good blackbodies to become available. As a result, much radiation work at the present time depends upon a blackbody reference when comparing specimens. Figures 2 and 3 show two types of apparatus using a blackbody reference. (2) In other cases, the blackbody has been used to calibrate a particular detector as that the signals from this detector may be converted directly into specific radiation data, whether it be emittance, reflectance, or absorptance data. Figure 4 represents such a technique whereby a calibrated detector is used for the measurement of total normal emittance. (2)

Some general comments concerning radiation are necessary in order to provide a common basis for further definitions or concepts. The thermal radiation being radiated from a unit area of an opaque solid (grey body) is a function of its temperature and of its emissivity. Emissivity is the ratio of the radiation from a certain material to the radiation from a blackbody at the same temperature.

This may be measured on a spectral basis or on a total basis. For the former, measurements would be made over a narrow wavelength increment at one time. Total emissivity would consist of the measurement of radiation over the entire wavelength region in which radiation would be present. The directional detection factor of emissivity is described by the terms normal and hemispherical where normal emissivity refers to only that radiation being emitted normal to the surface of the specimen while hemispherical emissivity would mean a measure of all radiation being emitted into the hemisphere bounded by the plane of the specimen.

The type of environment a particular spacecraft will encounter will determine the type of test conditions that may prevail. The usual protection for materials under test is a good vacuum (10^{-6} mm Hg). However, when the vehicle is not at consistently extreme high altitudes, it seems reasonable to assume that the test can be run in an air atmosphere. Likewise, where a material will be used in a vacuum, then testing in similar vacuum environments would be indicated. Inert atmospheres may be used when required. Most emittance measurements have been made either in air or in a vacuum. At present, the Aeronautical Systems Division is supporting programs in various laboratories for emittance measurements in an air atmosphere at temperatures up to 3000°F, in vacuum at temperatures up to the 4000° - 5000°F region, and in some cases, an inert atmosphere is used for specimen protection because of the endless variety of end requirements for such data.

Inherent to most experimental measurement programs is the problem of errors. An important probable source of error in emittance measurements is the uncertainty of specimen temperature. Although thermocouple contamination could result in a change of the calibration, the usual trouble is thermocouple location or thermocouple attachment including the problems of unpredictable temperature gradients. Some methods call for the thermocouple to be pressed against the front or rear surface of the specimen. Should the facility utilize an air atmosphere, the specimen could oxidize to such an extent that the thermocouple actually would be separated from the specimen indicating the temperature of the oxide layer. With a pressure type thermocouple in a protective atmosphere, changes in contact pressure caused by differential thermal expansion or spring failure may permit the thermocouple to move away from the specimen's surface. For metallic specimens where the thermocouple is welded directly to the specimen, care must be exercised to use the smallest wire feasible in order to minimize conductive heat losses. Larger thermocouple beads and wires can cause considerable cooling by conduction in the area of the bead. In this case, the true specimen temperature would be higher than indicated by the thermocouple output. The location of the thermocouple should be considered carefully. For thick specimens heated from the rear surface, it is natural that a temperature gradient from the rear to the front surface will be present. A thermocouple on the rear surface could indicate an erroneously high temperature because of the inherently higher temperature of the rear surface and because it could receive direct radiation from the heat source. A possible gradient from the middle to the edge of the specimen must be considered when locating the thermocouple on the front surface of the specimen. However, the furnace design would influence this type of a gradient. A related area of temperature measurement occurs in systems where the radiation from a specimen is compared directly with the

radiation from a blackbody. In such cases, it is essential that both furnaces (blackbody furnace and specimen furnace) be operating at the same temperature during the measurements.

Thus far, only opaque specimens have been considered. Many materials such as ceramics and ceramic coatings are translucent to infrared radiation from the heat source. Special precautions must be exercised, for should a cooling plate be moved into position between the heat source and the specimen just before emittance measurements are made, spurious radiation would reach the detector giving inaccurate readings.

Various techniques in use at this time provide for total normal emittance, total hemispherical emittance, and normal spectral emittance measurements in air, inert gas, or vacuum at temperatures up to the 4500°F region. With the various techniques or modifications thereof, many combinations of errors, both known and unknown, are encountered. In order to provide a firm basis for all emittance measurements of interest to the Air Force, this Directorate is supporting a program at the National Bureau of Standards to develop standard techniques for emittance measurements providing several sets of emittance standards to cover the range from low to high emittance. To better cover the spectral and temperature ranges, the spectral region has been divided into two parts - 0.7 to 15 microns and 15 to 35 microns. The temperature range has been divided into three parts: room temperature to 1000°F, 1000° to 2000°F, and 2000° to 4000°F. As the temperature of a body increases, the wavelength below 98% of the energy emitted by a blackbody will fall toward the shorter wavelengths (table 1). This indicates that at a very high temperature, the long wavelength emission will contribute only a small part of the total emission and emittance measurements in the 2000° to 4000°F temperature range, 15 to 35 micron spectral range are of less importance than the similar measurements in the 0.7 to 15 micron range.

The National Bureau of Standard program calls for the development and characterization of three emittance standards: low, intermediate, and high, for the overall region from 0.7 and 35 microns, and from room temperature to 4000°F. The first region to be studied will be from 0.7 to 15 microns, 1000° to 2000°F.

It was considered desirable as far as possible, that commercially available standard components be used when developing the standard instrumentation for emittance measurements. With this in mind, the National Bureau of Standards chose a double beam ratio recording infrared spectrometer. In its original operation, this instrument used a beam splitting device to divide into two equal and separate beams the radiation from a Nernst glower. The two beams were chopped alternately, 180° out of phase, and then passed through combining optics so that the two beams were transmitted along the same path, but at alternate intervals, through the monochromator into the detector assembly. The signals, corresponding to the two beams, were separated, amplified and rectified, giving two signals, each proportional to the intensity of its respective beam, which could be handled as desired.

Basically, this instrument was designed for transmittance measurements where a sample would be placed in one of the chopped beams and the two resulting signals would be compared to indicate the transmittance of the sample for particular wavelengths.

Since emittance is the ratio of energy emitted from a material to the energy emitted from a blackbody at the same temperature, it would be desirable to compare directly the energies from similar areas of the sample and from a blackbody at the same temperature. To define further the emittance as spectral, it is necessary to compare their energies

for narrow wavelength intervals. By removing the Nernst glower and the associated beam-splitting optics, two independent signals can be introduced and compared by the infrared spectrometer as shown in figure 5. This means that a blackbody furnace can be located so that its radiation will be the source of one beam for the spectrometer. The specimen furnace can be located so the radiation from the specimen will be the source of the other beam. It is necessary to insure that the optical paths are the same length and that the apertures are the same for these two beams. A differential thermocouple was installed with one junction in the blackbody furnace and the other junction in the specimen furnace so that the thermocouple output would indicate the magnitude, and direction, of temperature differences between the specimen and the blackbody. By feeding this thermocouple output into a center-zero potentiometer-controller, the power to one furnace can be controlled to maintain a temperature equal to that of the other furnace. This technique requires a simple independent temperature measurement to determine the temperatures of the specimen and the blackbody. This arrangement insures that all measurements from the specimen are compared with the blackbody at the same temperature. The remainder of the system is as originally designed where the two beams are chopped alternately, then combined before their introduction into the monochromator and the detector. As previously indicated, the signals from the detector are separated with respect to source and are amplified and rectified. The result is two d.c. signals that are proportional respectively to the radiation intensities from the specimen and the blackbody.

Of equal importance to the development of the standard techniques, is the development of the emittance standards themselves. Considerable time has been spent in selecting candidate materials for standards. Some materials were eliminated rather quickly on the basis of their temperature limitations. Naturally, the materials for standards must have melting points considerably above the temperature range for which they are to be used. In addition, the surface must be mechanically stable and temperature stable so that the emittance will not change appreciably with time and with temperature cycling. The National Bureau of Standards will recalibrate these standards periodically. Once these standards have been completely calibrated, they will be available from the Physics Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division, for short-term loan to those organizations having a bona fide need to calibrate their own emittance apparatus. These emittance standards will be prepared in an assortment of sizes and shapes to accommodate nearly all major laboratories making emittance measurements. However, changes in equipment design and the construction of new apparatus may result in size and shape requirements that will not be met by the standards now being prepared. In these cases, arrangements will be made with NBS to determine the feasibility of preparing a special set of standards.

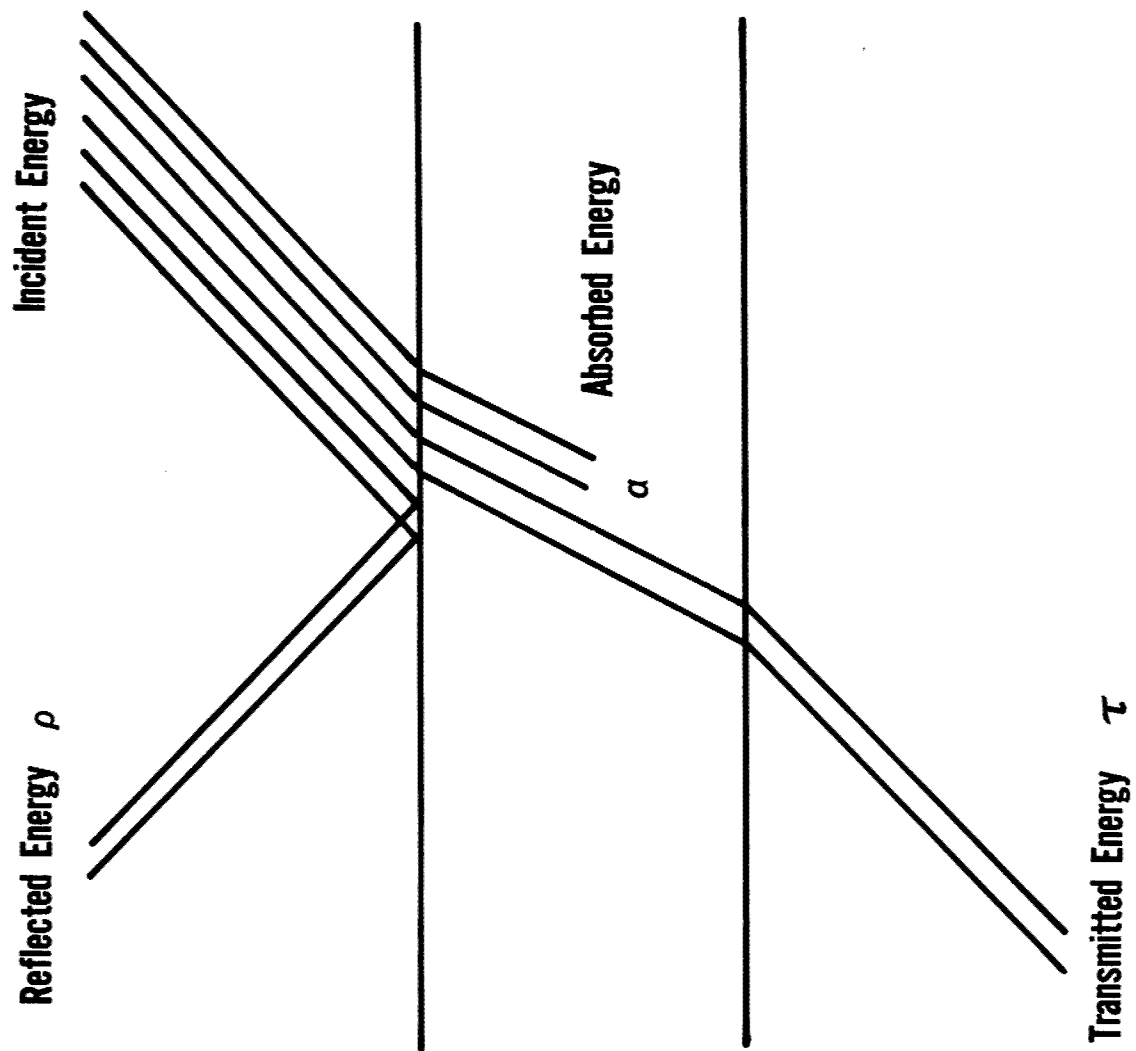
Since the National Bureau of Standards is responsible, primarily, for the development of standards and techniques of measurement, straight-forward emittance measurements on a wide variety of materials must be accomplished at commercial or university laboratories. In view of present technological developments, it is very important that emittance measurement capabilities for higher temperatures be available. NBS has been asked to continue their work on the higher temperature regions as previously indicated so that suitable standards will be available for laboratories making measurements in these extended temperature regions. Figure 6 shows (replotted on the same scale) the normal spectral emittance curves for oxidized Inconel and platinum at 2061°F (1400°K). These data were reported by National Bureau of Standards in WADD Technical Report 59-510. (3)

Thus far, greatest emphasis has been on emittance measurements, per se, of opaque solids. Recently a program has been initiated for the study of emittance for transparent and translucent materials. Although this program is relatively new, it is expected to yield information necessary for the thorough understanding of the general area of thermal radiation. Additional work is required to resolve the problem of total normal versus total hemispherical emittance data. Somewhat related to this area is the further investigation of emittance versus angle of emittance. Indications are that the Lambert Cosine Law does not apply for all types of surfaces and more information is needed before reliable predictions can be made regarding the angular emittances of a particular surface profile. At the present time, this Directorate is supporting a program to consider this problem; however, it is too early for conclusive results. Whenever the surface of a material is mentioned, the accurate description of this same surface comes to mind immediately. Earlier, it was stated that one problem in comparing earlier emittance data was the lack of a good uniform description of the surface. As in the humanities, what may be considered polished by one person may not be considered as qualifying for a "polished" label by another person. The effect of continued exposure at high temperatures or of surface conditions, on the emittance properties of specimens has been encountered. It now remains to evaluate these effects so that they may be dealt with effectively for the solution of continually arising technological problems.

In addition to the preceding outline of technological goals in this area, effort will be devoted to extending these measurements into the very high temperature regions and into the cryogenic regions as well.

BIBLIOGRAPHY

1. Worthing, A. G., "Temperature Radiation Emissivities and Emittances," Temperature, Its Measurement and Control in Science and Industry, American Institute of Physics, Rheinhold Publish.Corp. (1941)
2. Seban, R. A. and Rolling, R. E., Thermal Radiation Properties of Materials", WADD Technical Report 60-370, University of California
3. Harrison, W. N., Richmond, J. C., et al, "Standardization of Thermal Emittance Measurements", WADC Technical Report 59-510, National Bureau of Standards



GENERAL CASE FOR ENERGY TRANSFER

Figure 1.

U OF CALIFORNIA GIER - DUNKLE TYPE CAVITY

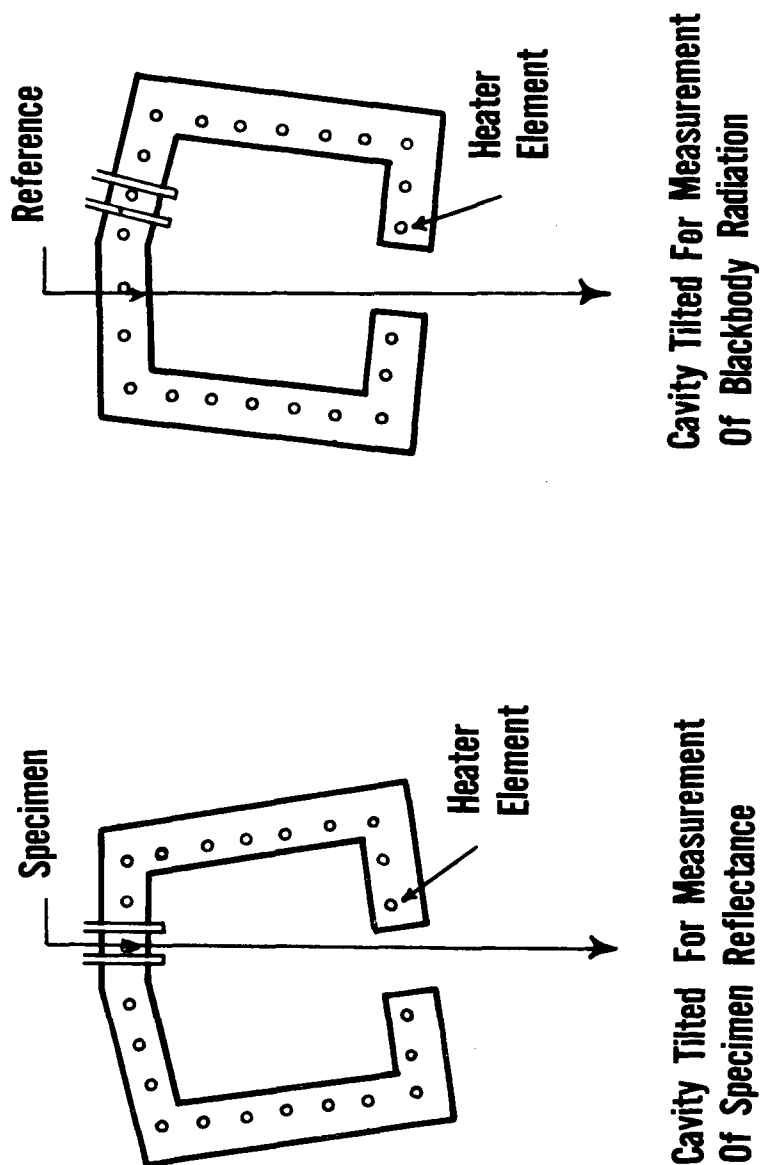


Figure 2.

APPARATUS FOR DETERMINING NORMAL SPECTRAL EMITTANCE

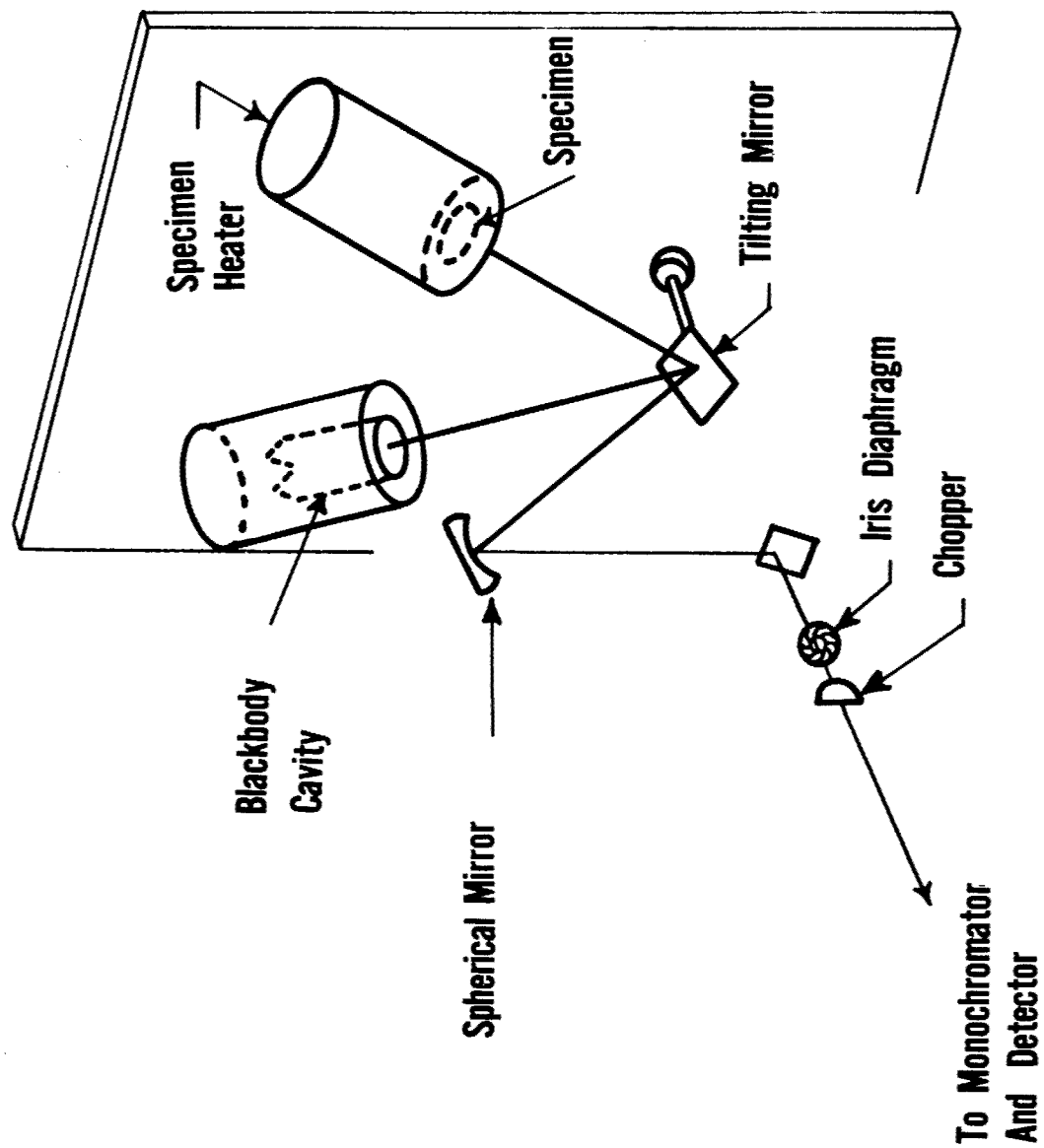


Figure 3.

APPARATUS FOR DETERMINING TOTAL NORMAL EMITTANCE (GAS-FIRED UNIT)

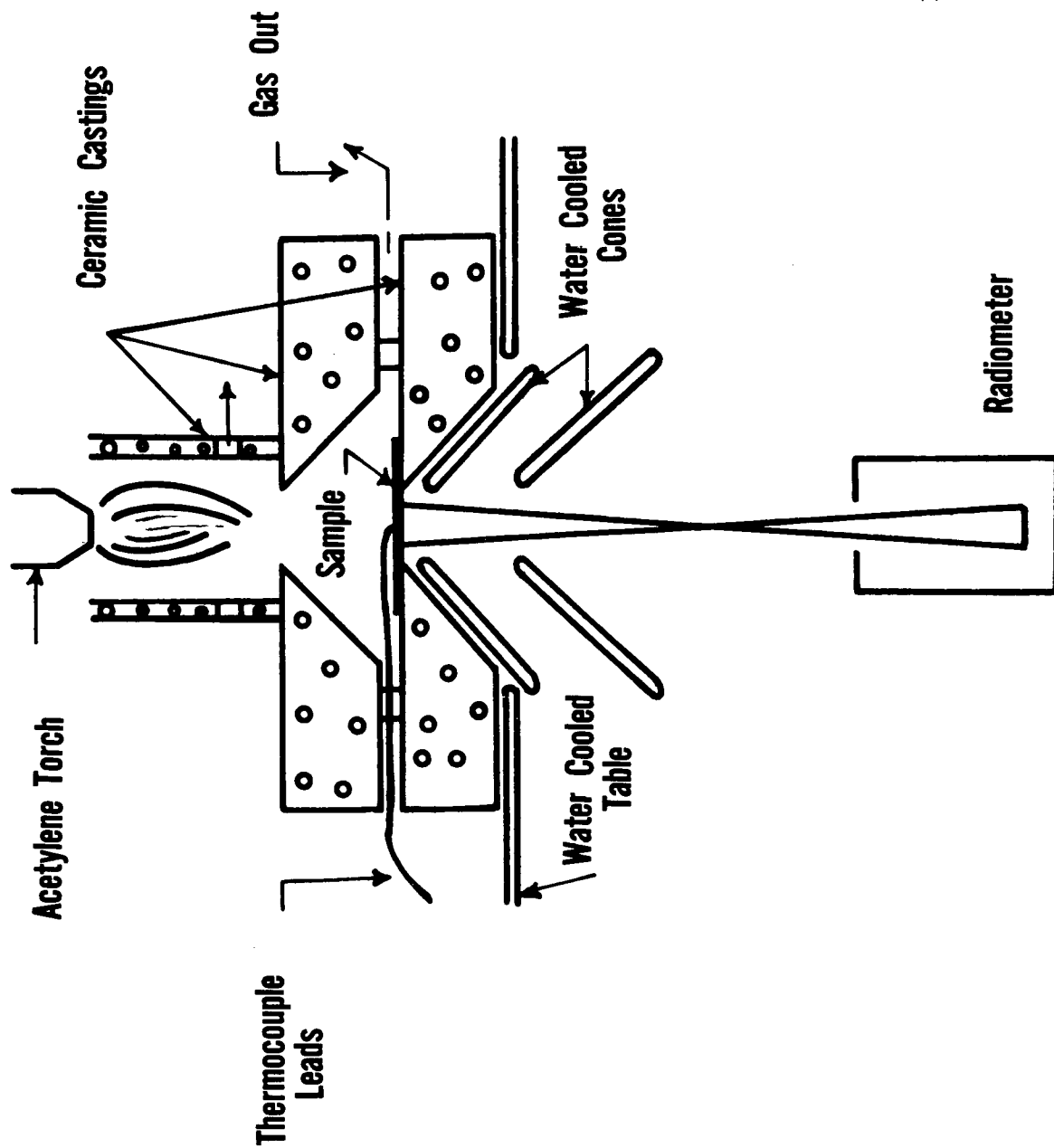


Figure 4.

SCHEMATIC DIAGRAM OF NBS APPARATUS TO DETERMINE SPECTRAL NORMAL EMITTANCE

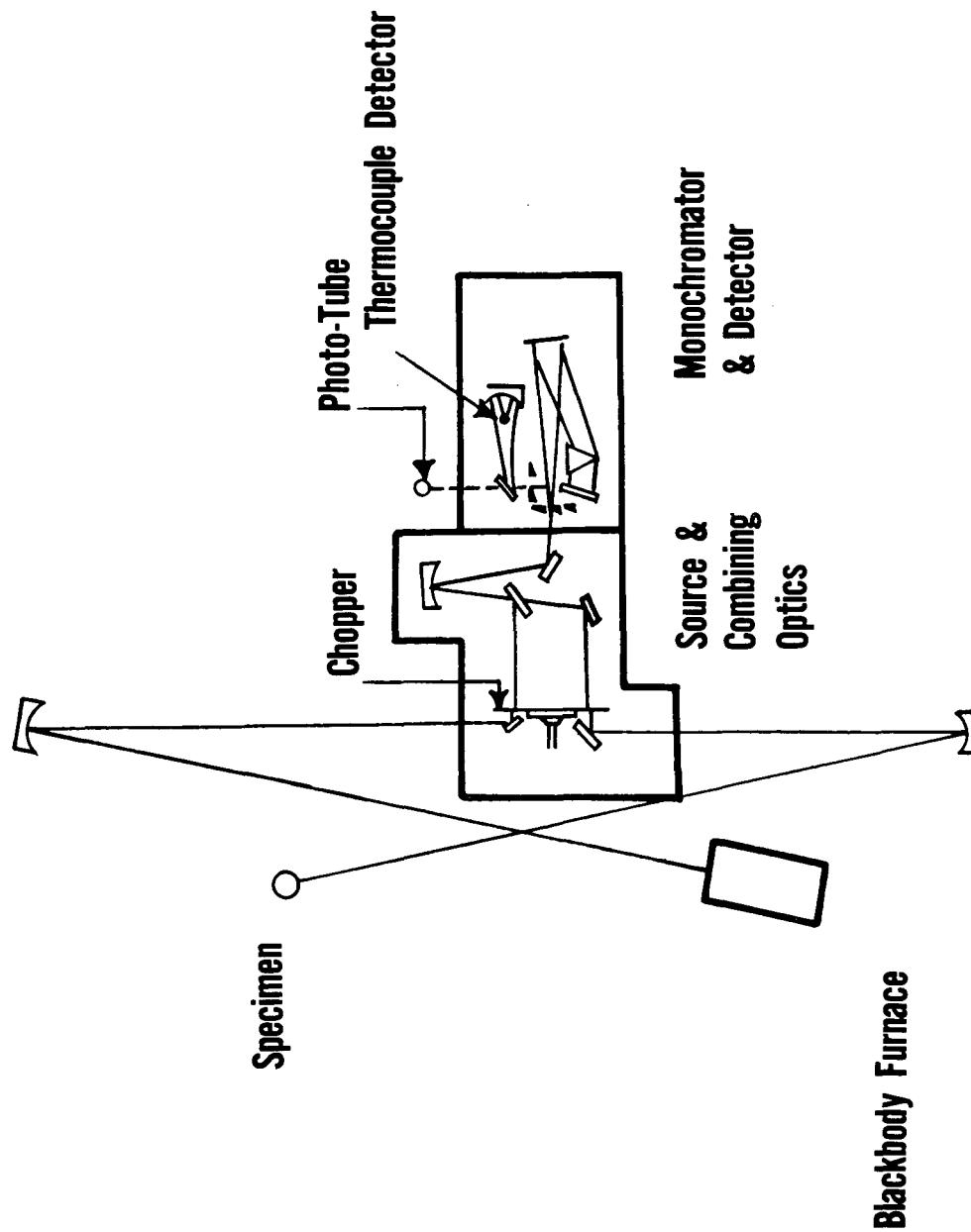


Figure 5.

NORMAL SPECTRAL EMITTANCE OF INCONEL & PLATINUM AT 2061°F (1400°K)

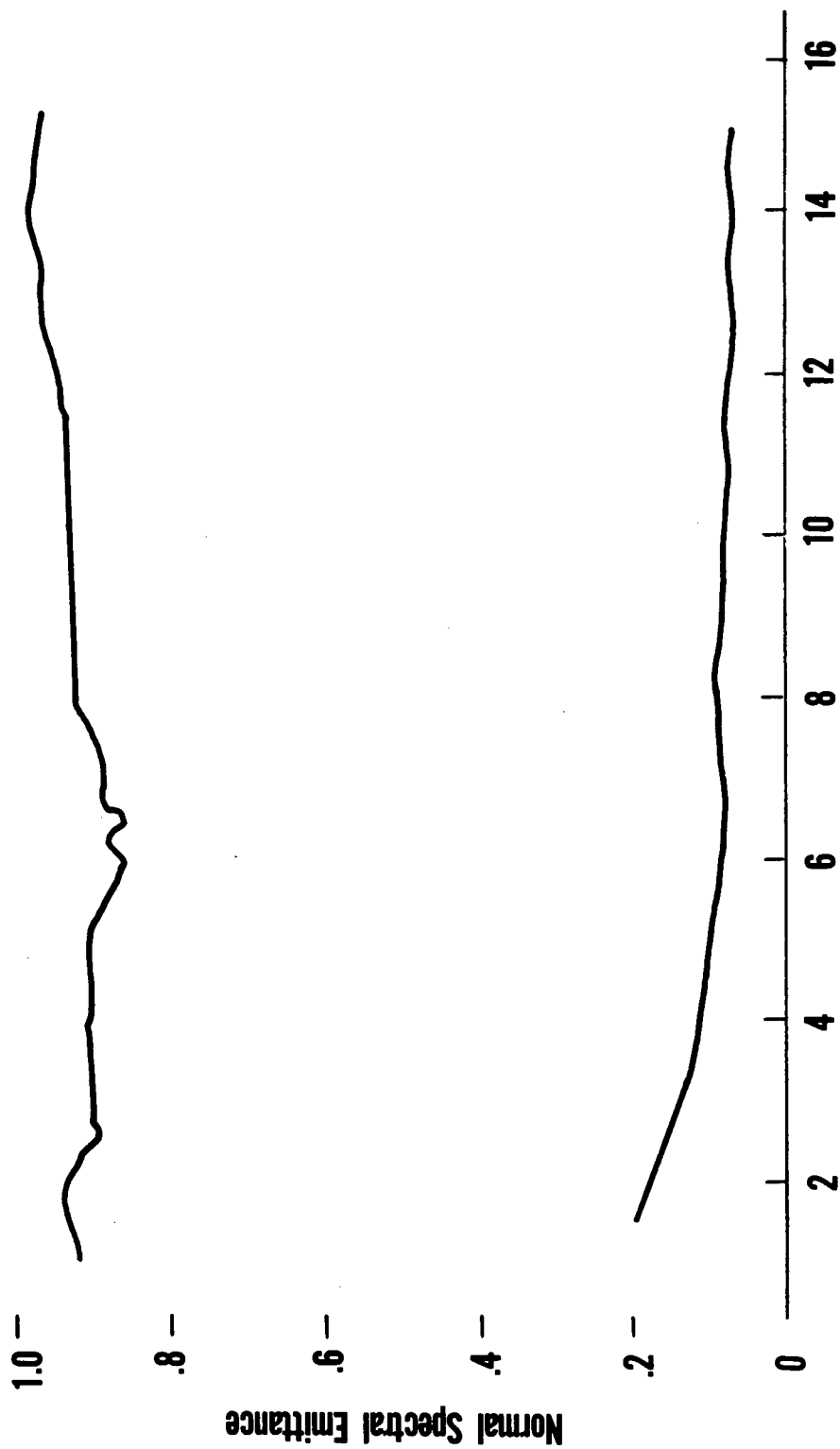


Figure 6.

ENVIRONMENTAL CONSIDERATIONS FOR THERMAL PROTECTIVE COATINGS

R.M. VanVliet

J.J. Mattice

Directorate of Materials and Processes, ASD

Introduction

As pointed out in accompanying papers, coatings and temperature control materials will have to survive and function reliably on and within space probes in a totally new environment when using thin films as coatings, we must consider the optical and physical changes which will result from long exposures to high vacuum, multiple forms of radiations, and elevated temperatures. This summary will point out those elements of space environment which are of chief concern to the proper performance of coatings and will consider the major interactions resulting from such exposure. The progress and challenges concerned with achieving reliable coating systems are reviewed. Some suggested approaches to potentially fruitful areas of study are emphasized.

Elements of the Space Environment

Figure 1 lists the environmental factors which may deteriorate outer surfaces of the space vehicle. Figure 2 illustrates the major problems encountered with all types of coating materials and outer surfaces when exposed to the high vacuum of space. It must be kept in mind that in space and in the transition region between the atmosphere and space, pressure or density factors are vectorial. The ARDC Model Atmosphere defines the upper layers of air with considerable precision for stationary vehicle. But the aerospace vehicle may be moving at orbital or escape velocities which are over 20 times as fast as the average gas molecule. Thus, the pressure on the front of the space vehicle may be quite high even in the rarefied upper atmosphere while the pressure to the rear is very low. When the space vehicle leaves the atmosphere, it must also contend with vectorial plasmas such as the solar wind or plasma (about 600 miles/sec) and high energy Van Allen radiation. In addition, the outgassing of the space vehicle itself may add significantly to the local environment. Thus, it is difficult to describe a precise vacuum condition for a space vehicle. While the definition of the vacuum environment may be difficult, many of the effects of this environment can be anticipated on the basis of terrestrial experiments.

The most obvious effect of vacuum is the evaporation or sublimation of high vapor pressure materials. The rate of vaporization of a homogeneous solid can be obtained from the Clausius-Clapeyron and Langmuir relationships as follows:

$$G = \frac{P}{17.14} \sqrt{\frac{M}{T}}$$

where:

G is the rate of evaporation in grams $\text{cm}^{-2} \text{sec}^{-1}$.

P is the equilibrium vapor pressure in mm of mercury.

M is the molecular weight of the gas.

T is the absolute temperature in $^{\circ}\text{K}$.

This equation can be used to compute the rate of evaporation of pure metals or pure compounds used as exterior coatings. For example, cadmium plating will evaporate at 44 mils per year if held at 260°F .

Dissociation and surface changes are important considerations in the performance of coating materials and will be discussed later as a function of the class of the material.

Intense radiation is the second major element of the space environment. For the purposes of this discussion we might divide these numerous radiation types into two broad classes; electromagnetic and particulate. Figure 3 outlines the various types and approximate fluxes of electromagnetic radiations. The electromagnetic component of cosmic radiation has low intensity and is rather inconsequential as far as coatings are concerned. When nuclear reactors are used in the space vehicle, gamma radiation of high energy may be present in large quantity and thus become an important consideration.

Soft x-rays are emitted in considerable intensity by the solar corona. The intensity is variable with solar activity ranging from 0.1 to 1.0 $\text{erg/cm}^2/\text{sec}$ at one astronomical unit (Earth distance). The solar x-rays vary in wavelength from about 1 to 100 angstroms.

The ultraviolet spectrum of the sun ranges from about 100\AA to 4000\AA . The vacuum and far ultraviolet radiation (see figure 3) is dominated by band emission and varies considerably with solar activity. There is also an ultraviolet continuum which extends into the vacuum and far ultraviolet but increases in intensity at longer wavelengths. The total intensity of this radiation is not accurately known but probably varies from about 20 to 50 $\text{ergs/cm}^2/\text{sec}$. No appreciable amount of this radiation penetrates the earth's atmosphere. The near ultraviolet ($2000\text{-}4000\text{\AA}$) has an intensity of about $10^5 \text{ ergs/cm}^2/\text{sec}$ or over 9 percent of the sun's energy. Virtually all the energy below 3000\AA and most of the energy between 3000 and 4000\AA is filtered out by the atmosphere as shown in figure 4. As a result, coatings may absorb 10 to 100 times as much ultraviolet light above the atmosphere as in the surface of the ground on a clear day. Thus the ultraviolet light is definitely the most serious radiation problem particularly in the case of organic coatings.

About one third of the sun's energy is in the visible and most of the balance is in the near infrared to $30,000\text{\AA}$ or 3.0 microns. The absorption of this energy determines the primary heat input to the satellite or space probe. The heat from the earth, satellites, and other low temperature bodies is radiated primarily at wavelengths greater than 3 microns. Microwaves and radiowaves are at longer wavelengths and are radiated at low intensity by all celestial bodies and by the interaction gas and plasmas in space. The sun and other stars radiate radiowaves at high but variable intensity.

The second major type of radiation is particulate in nature and is illustrated in figure 5. The cosmic component of this radiation consists of the highest energy particles or ions. The bulk of the cosmic radiation is protons with small quantities of heavier nuclei.

When this radiation and the accompanying electrons are trapped in the Earth's magnetic field, it is known as Van Allen radiation. The low energy electrons in the Van Allen belt are rated as a potentially serious materials problem with effects similar to ultraviolet, but the absorption of this radiation is believed to be relatively low.

The solar magnetic field continuously ejects a hydrogen plasma known as the solar wind. This plasma is believed to have a temperature of 220,000°K or 26 ev upon reaching the earth. This is about equal in intensity to solar x-rays. Little is known about the effect of this plasma on coatings.

Neutrons are associated with reactors and would pose many problems where reactors are used for power generation. On the other hand, alpha particles are of minor concern since their penetration is slight.

Micrometeorites or space debris forms the third element of the space environment. This was considered a major hazard of space flight until the actual launching of satellites. Now it is tentatively classed only as a long term hazard comparable to some of the milder radiation effects, in altering the properties of coatings.

Organic Thin Films and the Space Environment

The Problem of Vacuum

Many writers have stated that the greatly reduced pressure of the space environment makes the use of organic polymers as plastics and films impractical because of sublimation. It is now reasonably clear that a given polymer will not volatilize as a result of vacuum alone. Residual lower molecular weight species present as a result of incomplete polymerization, are often responsible for observed outgassing of polymer films. Therefore, the vacuum is no real problem when considered by itself provided the polymeric material is reasonably high in molecular weight and free of lightweight components (obviously an idealized situation).

The above points illustrate where a good deal of effort could be directed. Little work has been done on the basic film forming polymers to optimize the properties of flexibility, toughness, and adhesion, where the polymer must be used as is. Specifically, further study should include the development of polymer systems which are internally plasticized and the preparation of low molecular weight plasticizers which have little tendency to volatilize when dispersed in a film. That low molecular weight compounds may be retained in a polymeric substrate may be seen from figure 6. In this case, a class of polyhydroxybenzophenones is shown to diverge from the well known Henry's Law. The low volatility of these compounds is the result of hydrogen-bonding to electronegative centers in the polymer chains. For high vacuum applications where a plasticizer is required, new materials which act in a similar manner if severe outgassing is to be avoided will have to be made available.

In many cases the broad molecular weight distribution of polymers may be a limiting factor. However, figure 7 shows how one polymer, poly- α -methylstyrene, may differ in molecular weight distribution as a function of initiation method. The latter sedimentation pattern shows that nearly mono-disperse material may be obtained when the polymerization technique is directed towards this end. It is highly probable that modification of existing techniques, along with the development of novel ones would lead to the availability of a number of common film forming polymers of very narrow molecular weight distribution. Such materials might then be used to prepare films with a very low concentration of lightweight components.

Vacuum and Temperature Combined

Figure 8 lists a number of general classes of film forming resins and the gross changes usually observed when these materials are exposed to temperature in vacuum. It can be seen that at present no unmodified organic films are available for extended application over 500°F. Performance of even the silicone at this temperature is marginal due to cracking and adhesional failures. Again, however, the polymer chemist has provided a possible answer in the form of several new promising raw polymers with enhanced thermal stability. Some of these are listed in figure 9. Adaptation of these materials to useful, thermally stable films is one of the tasks of the industrial research laboratory. The Air Force needs temperature resistant basic resins with good physical and color stability. Base polymers with these properties and capable of low temperature cure are also in demand.

Additional basic and applied research are required to define and improve properties of the new materials. We should study these materials quantitatively in terms of degradation mechanism and kinetics under oxidative and non-oxidative conditions. Such studies should be carried out both in the finely divided and thin film states.

A stable and useful 1000°F organic film forming material is a reasonable goal for the relatively near future.

Nuclear Radiation Interactions

The impingement of ionizing radiation in high doses on organic thin films will also result in physical, chemical, and optical changes. However, for exposure to all elements of the space environment, nuclear radiation is not so severe a problem area when compared to the ultraviolet flux. Further, degradative processes operating within solid organic films do not result in a degree of damage comparable to that experienced with fluids, greases, or elastomers. In many cases film properties are enhanced by more complete crosslinking (thus possibly leading to reduced volatilization). Severe failure of films in the laboratory due to ionizing radiation has seldom been observed with the proper choice of polymeric starting materials.

A possible exception to the above statements may be found in the interaction of low energy electrons with organic materials. A considerable flux of this type of radiation, with energies on the order 20 to 200 Kev, as opposed to several Mev has been detected in the earth's magnetic belts. The extent of this potential problem concerning organic films or any other physical class of organic materials has not been defined. Certainly, work should be carried out to define the magnitude of any problem which might exist. Should one become evident, necessary research into degradation mechanism, mode of stabilization, and development of resistant materials should be undertaken.

Considerable effort has been expended in an attempt to understand the mechanism of stabilization of resonant structures to nuclear radiation. One can now predict with some measure of success the resistance of polymeric materials from the structure and aromaticity of the system. These empirical relationships have occasionally been carried over into the ultraviolet radiation problem. It should be kept in mind, however, that the discrete processes of energy absorption, stabilization, and dissipation are quite different for nuclear and ultraviolet radiation. As a result, the presence of highly resonant structures is a very poor measure of the ultraviolet stability of a polymer film.

There are a very few classes of organic compounds exhibiting high absorption and low rate of reaction (a high rate would be expected) to ultraviolet light. These compounds have not been observed to undergo fluorescence or phosphorescence, as do most nuclear radiation stable materials. This very intriguing fact emphasizes the point that one must be very careful in drawing analogies between ultraviolet and nuclear radiation interactions with organic materials.

The Ultraviolet Radiation Problem

The most severe environmental factor we must consider for organic thin films which are to be used as the basis for temperature control systems in space is the ultraviolet radiation which is present above the earth's atmosphere. The reasons for the severity of this problem are many but may be stated generally as follows:

1. The ultraviolet radiant flux in space is very intense, especially in the wavelength region 2000-4000Å.
2. This same 2000-4000Å region is the primary absorption region for common electron rich bonds such as are found in useful polymeric materials. This may be seen for a typical polyester film in figure 10. Note the decreased intensity and short wavelength cut off for the same polymer in July and December within the atmosphere.
3. The energy per photon in this region exceeds the energy of typical bonds, thus making polymer breakdown a distinct possibility.
4. Photochemically induced changes or degradations result in the shifting of absorption bands toward or further into the visible region. This condition leads to a shifted temperature balance of the substrate due to higher energy absorption.
5. The few film forming polymers which do not inherently absorb ultraviolet light, and therefore should not degrade, are observed to decompose nevertheless due to the photosensitizing (or catalytic) action of impurities which apparently are universally present.

A few basic polymers do exhibit a degree of inherent photochemical stability. One of these is pure melamine formaldehyde, a poor film former. However, even if practical difficulties could be overcome, the finite rate of change, as indicated in figure 11, still prevents use of polymers alone for long term applications which will be required in increasing numbers in the future.

The weight of this evidence would seem to indicate it is inadvisable to consider further polymer films as substrates for temperature control systems. However, as an outgrowth of studies conducted to produce stable polymers in air, a growing volume of data indicates that for many applications certain additives will prevent deterioration of physical and optical properties for an extended time period in the space environment. The technique of incorporating stabilizing additives (U. V. absorbers) does not detract from the fundamental contributions which still need to be made regarding the little known chemistry and mechanism of photosensitization and photodegradation of polymers films. Little, however, can be learned in studying commercially available materials from a fundamental point of view. Specialized polymerizations utilizing high purity reagents are necessary if quantitative mechanistic data are to be obtained.

Organic Coatings For Use in the Space Environment

Within the last two years the magnitude of the ultraviolet problem concerning organic temperature control coatings, stimulated considerable effort aimed toward a feasible solution. Several important achievements under Air Force sponsored contractual efforts have paved the way to realization of this goal. Some brief highlights include:

1. Vapor pressure studies conclusively demonstrating the protective additives are compatible with the high vacuum of space (see the work of Schmitt and Hirt, WADC TR 59-354).
2. Successful synthesis of "metallocene" based protective absorbers. Figure 12 points out some structures which have been synthesized and figure 13 shows how one is effective in protecting a silicone alkyd film.
3. The feasibility of utilizing unpigmented, wholly organic absorbing systems for a wide range of stable temperature control systems not requiring high temperature stability.

The above areas are presently in various research stages and much work needs to be done. For example, with the availability of new polymer additives, applied effort should be expended to elucidate what specific effects, if any, are manifested by these materials in the formulation and curing of the systems to which they are applied. The thermal stabilities of certain coating systems may be increased or decreased by incorporation of novel materials.

Within the last few years a number of "U. V. radiation effects" studies have been initiated under Government sponsorship and by Industry. For some applications an ultraviolet protective coating system might be applied to prevent physical deterioration of various classes of materials. Structural plastics, which are presently being used and being considered for a host of future space ventures are a case in point. The use of thin covering films would allow the designer to formulate structural members to optimize strength and prevent incorporating large amounts of stabilizing additives into the entire bulk material. Other examples where such protective systems may be employed are textiles and elastomers used in situations where ultraviolet radiation causes damage.

Limitations of Present State of the Art

The temperature limitation of available film forming polymers has been discussed. In addition, when the temperature control application is considered, stable coating formulations with low initial solar absorption are non-existent. More simply, there are presently no thermally and ultraviolet radiation stable usable resins which are visibly colorless. Further, all high stability additives thus far established are colored in the visible (and consequently absorb solar radiation for which the eye is a reasonably good detector).

One must then conclude that presently there are not available temperature control systems which can provide very cold surfaces in space, such as might be achieved by the use of a white-pigmented, colorless, organic resin. Such a system would provide high reflectance to incident energy, low absorption, and very high emittance at long wavelengths for the small amount of energy that is absorbed. Organic coatings are by nature most easily prepared to meet these requirements. Such systems, if available for long term use, would find wide variety of specialized applications.

It should be evident that there is wide latitude for contribution by non-Government research organizations to Air Force materials requirements which are concerned with the adaptability of organic coatings to the space environment.

Inorganic Coatings in the Space Environment

At first glance, the effects of the space environment on inorganic coatings would appear to be a minor consideration. But further consideration places rather severe restrictions on certain inorganic coatings for applications that are routine in a terrestrial environment. However, most of the environmental effects have been only partially explored or merely postulated. Some of these data and postulations are assembled below and in figures 14 and 16.

Ceramic and Anodic Coatings

The evaporation of ceramic and anodic coatings may pose a problem where these coatings are used for high temperature heat radiators. Since this is the most important use of ceramics in direct exposure to space, it deserves further consideration.

Probably the most serious evaporation problem uncovered to date is that associated with the oxides of chromium. Since the prime protective layer on the stainless steels and super alloys is based on chromium oxide, air or chemically oxidized coatings on these alloys will have only limited utility in space. Chromium oxide dissociates at about 780°C and the higher vapor pressure chromium is the primary evaporated specie. At lower temperature the oxides of chromium evaporate at a slower rate. This evaporation apparently takes place slowly even at temperature as low as 600°C. This is unfortunate because oxide films on chromium alloys are one of the best and most easily formed high emittance coatings. A chemical process which would provide a stable emissive coating on the super alloys is seriously needed.

Many oxides are rendered more volatile by their environment. Alumina, in the presence of tantalum will evaporate at a much lower temperature because of the reduction of the alumina. Silica can also be reduced to the more volatile silicon monoxide by the presence of carbon and other materials. As a result of these findings, possible reduction reactions will have to be considered for high temperature vacuum operations where the inorganic compound exists in a more volatile, lower oxidation state.

Dissociation may be promoted by ionizing radiation at high temperature. The ionizing radiation might be the high intensity solar ultraviolet light or nuclear radiation from reactor power systems. Since an effective radiator coating is essential to the operation of nuclear and other power plants in space this vital area urgently needs exploration.

Another unexplored area is the effect of vacuum on adherence and thermal shock resistance of ceramic coatings. It is well known that non-oxidizing atmospheres during firing can cause the "dewetting" of a porcelain enamel from its metal substrate. It appears probable that this dewetting action might cause loss of bond in high temperature-vacuum exposure unless the ceramic is specifically designed and tested for this application.

Ceramic and anodic coatings are not necessarily free from ultraviolet effects even at room temperature. Figure 15 shows the effect of ultraviolet light on the reflectance of anodized aluminum. Similar effects have been reported for titanium dioxide opacified inorganic coatings. These changes are due to the formation of F and V centers (negative

or positive vacancies, respectively) in the coating and may be caused by ultraviolet light absorbing impurities such as iron oxide. These changes increase the temperature of the space vehicle in a manner similar to that of an organic coating that yellows due to ultraviolet light degradation.

The formation of vacancies has no significant effect on the emittance of coating, i.e., its power to radiate heat. However, the loss of water of hydration can seriously lower the emittance of the coating. Occasionally, crystal change will have similar effects. Thus, a combination of increased absorption of solar energy and decreased emittance at long wavelengths could cause a very large increase in temperature of a space vehicle.

Diffusion can have a dramatic effect on the reflectance, emittance, and other properties of oxide films in a vacuum. Some metals such as titanium permit the diffusion of oxygen at high temperature. Thus the oxide film on titanium could gradually disappear by diffusion into the metal.

Similarly, metals may diffuse through the oxide film to the surface at high temperature. In the atmosphere, this diffusion is not evident because the metal oxidizes as rapidly as it reaches the surface. In a vacuum, oxidation would not take place and considerable reduction in the emittance of the coating might occur. Since diffusion through the high vacancy concentration in iron and chromium oxides has been demonstrated, this phenomena requires further investigation.

The Metallic Film

Figure 16 outlines the effects of the space environment on metal surfaces. The effect of evaporation mentioned before is not necessarily a simple one. The evaporation of chromium from a rough stainless steel surface is reported to have a smoothing or polishing effect leaving a mirror like surface. On the other hand, mirror surfaces of silver undergo thermal etching to give a finely roughened surface after vacuum-thermal exposure.

Computation of the evaporation rate of metal films is frequently complicated by inaccurate or inadequate data. This is particularly true of metals such as aluminum which form tight, adherent, refractory oxide films. Since a very thin layer of metal oxide can virtually stop metal evaporation, data for metals such as aluminum is very difficult to obtain. The rate constants for metal evaporation is generally approximated by extrapolating vapor pressure data from the Clausius-Clapeyron equation. Many references have ignored the fact that data taken in the liquid state cannot be used directly to plot vapor pressures in the solid state. This leads to inaccurate evaporation rates. Cadmium and chromium probably pose the most serious evaporation problem of commonly used metal coatings. For some applications metals may require coatings to prevent evaporation.

Sputtering will be a serious problem for exterior metal coatings subject to long space exposures. Sputtering not only causes loss of material but may also change the metal surface characteristics. Proton sputtering will be a problem on all extended space flights due to the solar wind. Both proton and electron sputtering will be prevalent in the concentrated areas of the Van Allen radiation belt. The yield of metal sputtered, increases with increasing ion energy. Oblique ion impacts generally give higher sputtering yields up to 50 to 60 degrees from the normal. Some metals such as gold and silver develop rough surfaces during sputtering. The yield varies markedly with the filling of the d-electron orbitals. Aluminum has the best resistance to sputtering of the reflective

metals. Some of the refractory metal oxides such as alumina and titania have better resistance than the parent metal but this area needs much more study.

Changes in optical properties of metal coatings are important in space vehicle temperature control and mirrors used to concentrate solar energy. These optical surfaces may be destroyed by micrometeorites, sputtering, and evaporation. The degree of damage to the surface will vary with the type of metal, the temperature, and the eroding media. Much more information is needed on these effects. In some cases, a transparent organic or inorganic top coat may ease the problem.

Some metals undergo severe creep at high temperature upon extended exposure to vacuum. This phenomenon has been only partially explored. One approach is to coat the metal with another coating that is more ductile at high temperature. This would insulate the metal from the vacuum environment.

The short circuiting of insulators by the vacuum evaporation of metals has already been noted. The vacuum deposition of volatile metals can also effect heat transfer and other surface properties such as friction.

Summary

Although a knowledge of the properties of materials allows one to compound temperature control systems on paper to prescribed requirements, long term use of many such formulations will lead to deterioration of physical and optical properties, and thus, to altered temperature balances. Conducting effective research to overcome these problems has been hampered by insufficient information about some factors of the space environment. Further, many of the environmental "effects" under study are still only postulated and little is known of the resultant optical and physical changes which will occur should they be proven valid.

Therefore, a large number of research areas are open to further study and clarification. Full Government-Industry cooperation is necessary, successfully to resolve the many problems that confront us.

BIBLIOGRAPHY

1. ASD TN 61-72 "Organic Coatings for Control of Spacecraft Temperatures," R.M. Van Vliet, 1961.
2. ASD TR 61-5 "Development of Heat Barrier Coatings," American Machine and Foundry Co., 1961.
3. ASD TR 61-151 "Reflective Inorganic Coatings," Georgia Institute of Technology, 1961.
4. WADD TR 61-108 "Synthesis of Metal-Cyclopentadienyl Derivatives for Use as Ultraviolet Absorbers," Wyandotte Chemical Corp., 1961.
5. WADD TR 60-704 "Studies on the Protective Ultraviolet Absorbers in High Vacuum Environment," Part II, American Cynamid Co., Feb. 1960.
6. WADD TR 60-773 "Proceedings of Symposium Coatings for the Aerospace Environment," 1960.
7. WADD TR 60-386 "Spectrally Selective Coatings for Temperature Control of Space Probes," R.M. Van Vliet, Oct. 1960.
8. WADD TR 60-703 "The Ultraviolet Degradation of Organic Coatings," Part I "Degradation in Air," Part II "Degradation in Vacuum," U. S. Naval Research Laboratory, Oct. 1960.
9. WADD TR 60-317 "Development of Ceramic Coatings with Controlled Reflective and Emissive Control Properties," A.D. Little, July 1960.
10. WADD TR 60-126 "The Vacuum-Thermal Stability of Organic Coating Materials," Part I. "The Polyurethanes," Lt. Mattice, 28 Oct. 1960.
11. WADC TR 59-268 "Vacuum Volatility of Organic Resins," Lt. G.F. Matacek, 23 Sep. 1959.
12. WADC TR 57-334 "Evaluation of the Mechanisms Which Affect the Performance of Thermal Radiation Resistance Coatings," Armour Research Foundation of Ill. Inst. of Tech. 18 April 1958.

1. Vacuum
 Vectorial Effects
2. Radiation
3. Micrometeorites

Figure 1. Space Environmental Agents

1. Evaporation
 Surface Controlled
 Diffusion Controlled
2. Dissociation
3. Complex Changes Affecting Surface Temperature

Figure 2. Gross Vacuum Interactions

1. High Energy
 Cosmic-low total energy
 Gamma-reactors
2. Soft X-rays
 0.1 ergs/cm², variable
3. Ultraviolet

Far U.V. 100-1200A	10 ergs/cm ²
Vacuum U.V. 1200-2000A	20-30 ergs/cm ²
Near U.V. 2000-4000A	10 ⁵ ergs/cm ²
4. Visible
 One Third of the Sun's Energy
5. Infrared
6. Radiowaves

Figure 3. Electromagnetic Radiation

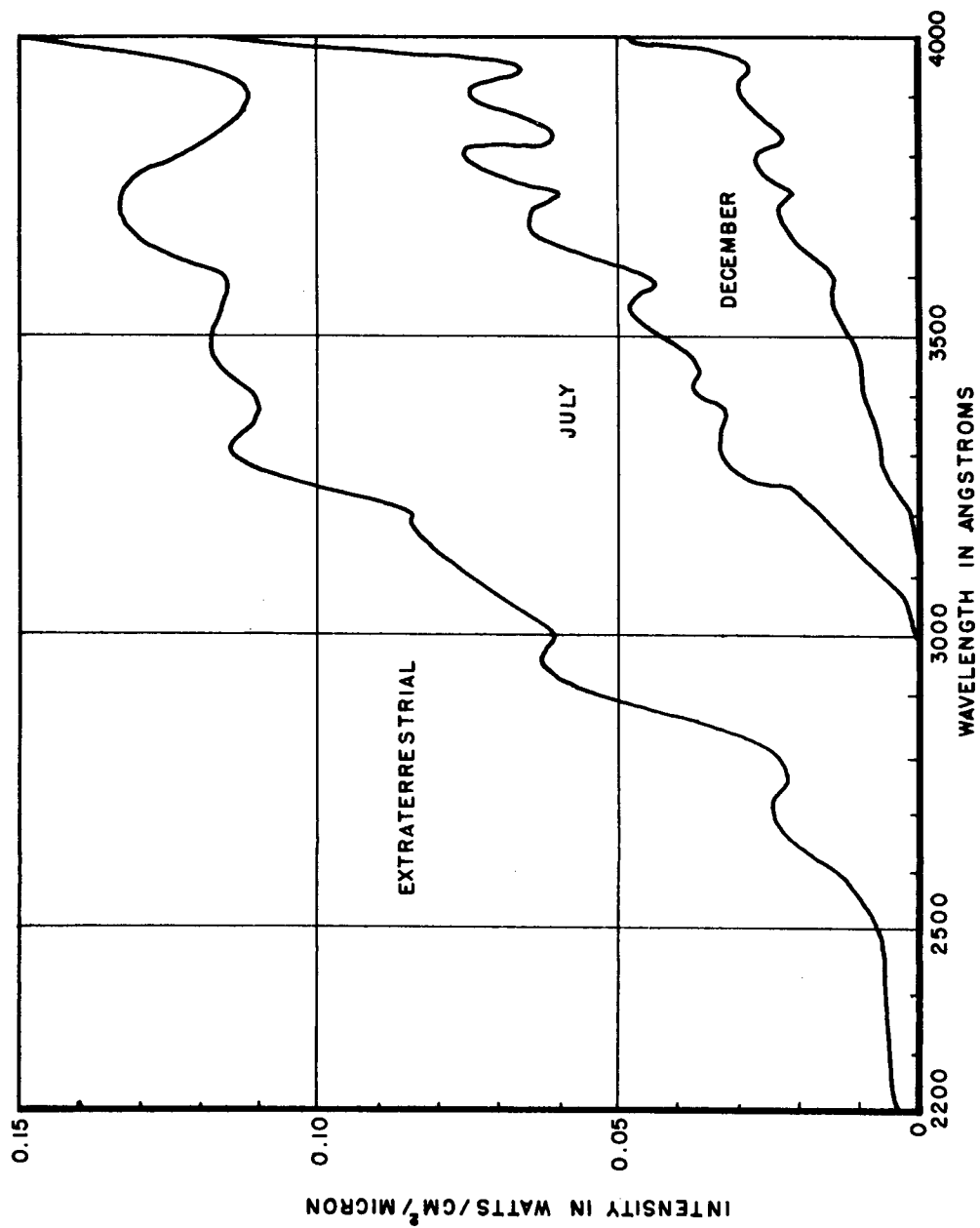


Figure 4. Spectral Distribution of Ultraviolet Light in Space and on Earth

1. Cosmic-low total energy
2. Van Allen Radiation
 - Protons-low total energy
 - Electrons-maximum about 3000 ergs/cm²/sec
3. Solar Wind-Proton component about 0.4 ergs/cm²/sec
4. Neutrons, alpha particles

Figure 5. Particulate Radiation

Rate in g/cm ² /day	T, °C	Condition
5.4×10^{-5}	25	Pure Compound
1.6×10^{-10}	25	3.4% dispersed in cellulose acetate film

After Schmitt and Hirt, WADD TR 60-704, July 1960

Figure 6. Volatility of 2,2' - Dihydroxy - 4-Methoxybenzophenone in Vacuum

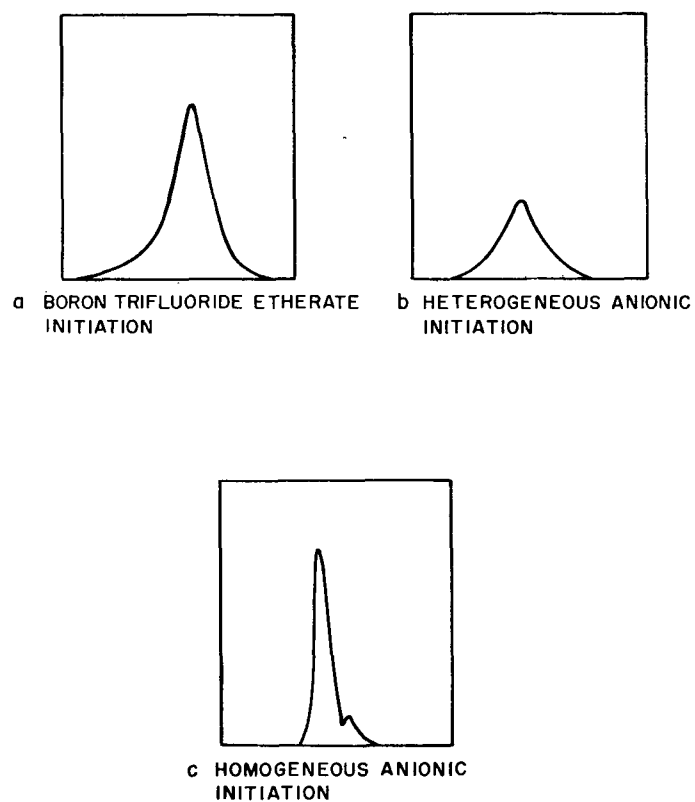


Figure 7. Sedimentation Patterns for Poly- α -Methylstyrene; after Fox & Isaacs, U. S. Naval Research Laboratory, Report 5518, August 1960

Class	Approximate Temp. Limit, °F	Physical Changes
Epoxy	400	Severe wt. loss
Silicone	500	Cracking, lost adhesion
Polyurethane	350	Severe wt. loss, yellowing
Polyester	350	Severe wt. loss, yellowing
Phenolic	450	Blackening
Vinyls	400	Severe wt. loss, flaking

After Matacek, WADC TR 59-268
and Mattice, WADC TR 60-126

Figure 8. Limitations of Common Film Forming Resins in Vacuum

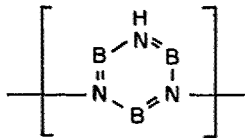
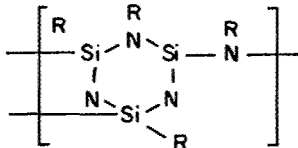
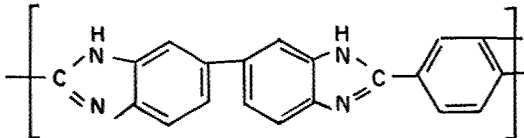
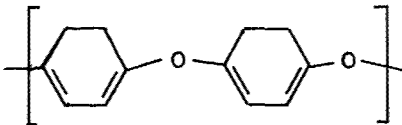
Class	Basic Chemical Structure	Potential Useful Temperature Range
Borazoles		1500°F
Silazines		800°F
Benzimidazoles		1000°F
Polyethers		700°F

Figure 9. Promising New Classes of High Temperature Polymers for use as Coating Resins

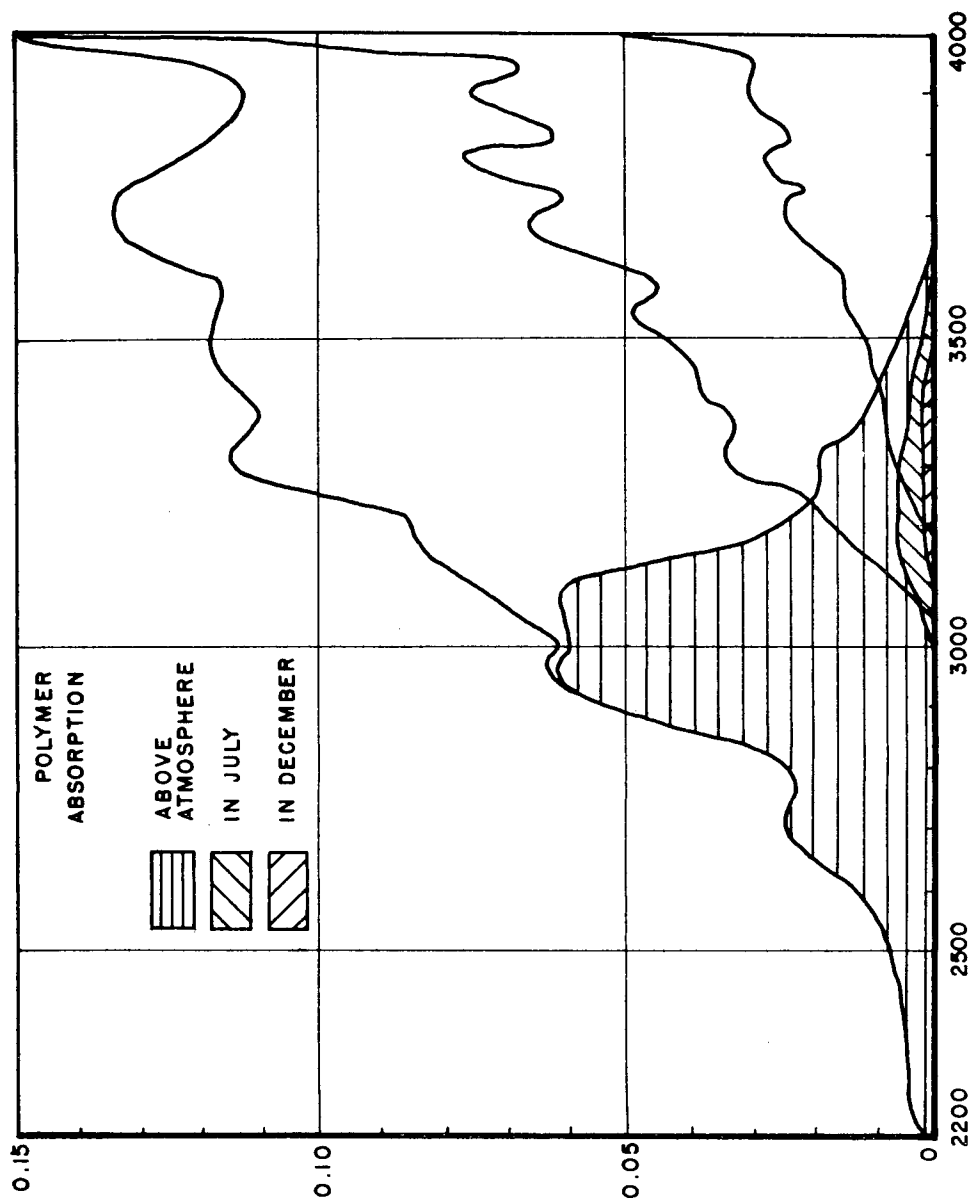


Figure 10. The Ultraviolet Energy Absorbed by a 0.0025 cm Film of Polyethylene Terephthalate when Exposed to Sunlight under Terrestrial and Space Conditions

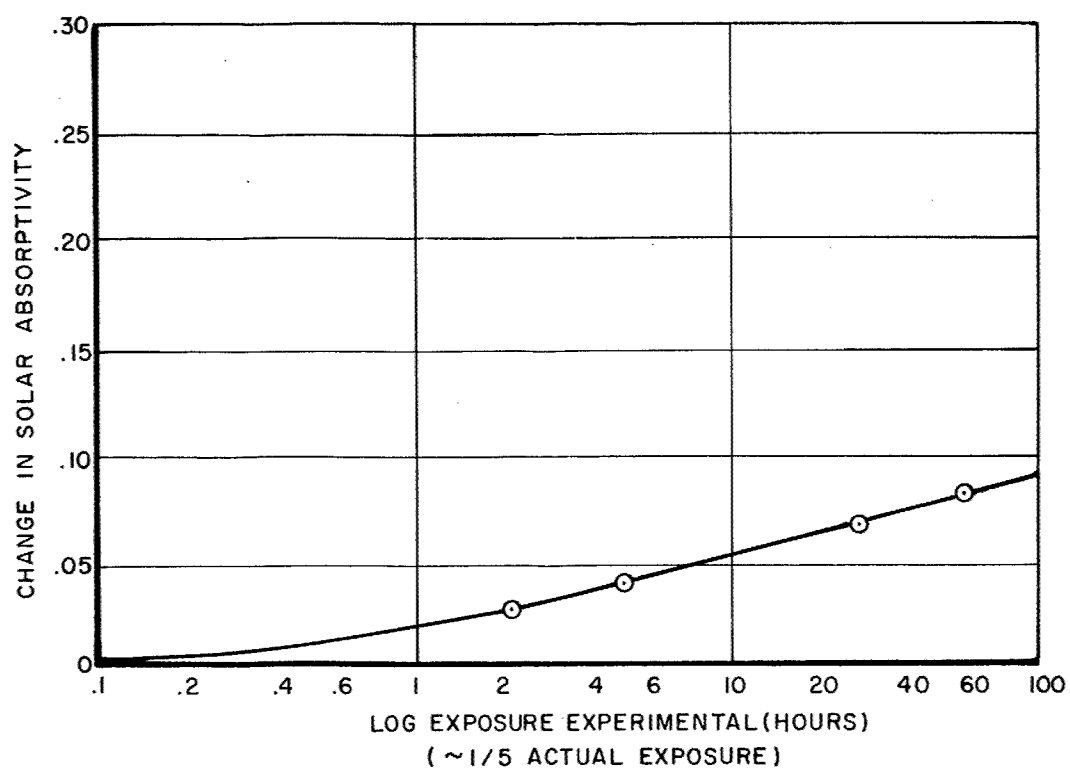
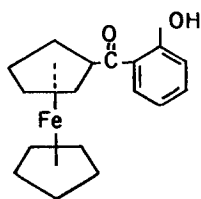


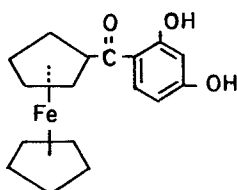
Figure 11. Increased Absorption of Melamine Formaldehyde, a "Stable" Polymer
After Schmitt and Hirt, 7th Quarterly Progress Report, Contract AF 33(616)
5945, October 1960

STRUCTURE

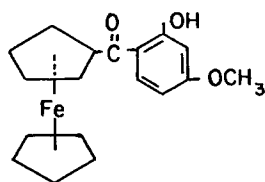
NAME



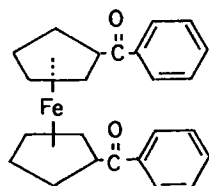
2-hydroxybenzoyl ferrocene (HBF)



2,4-dihydroxybenzoyl ferrocene



2-hydroxy-4-methoxy benzoylferrocene



1,1' -dibenzoylferrocene

Figure 12. Metallocene U. V. Absorbers
After Schaaf, WADD TR 61-108, April 1961.

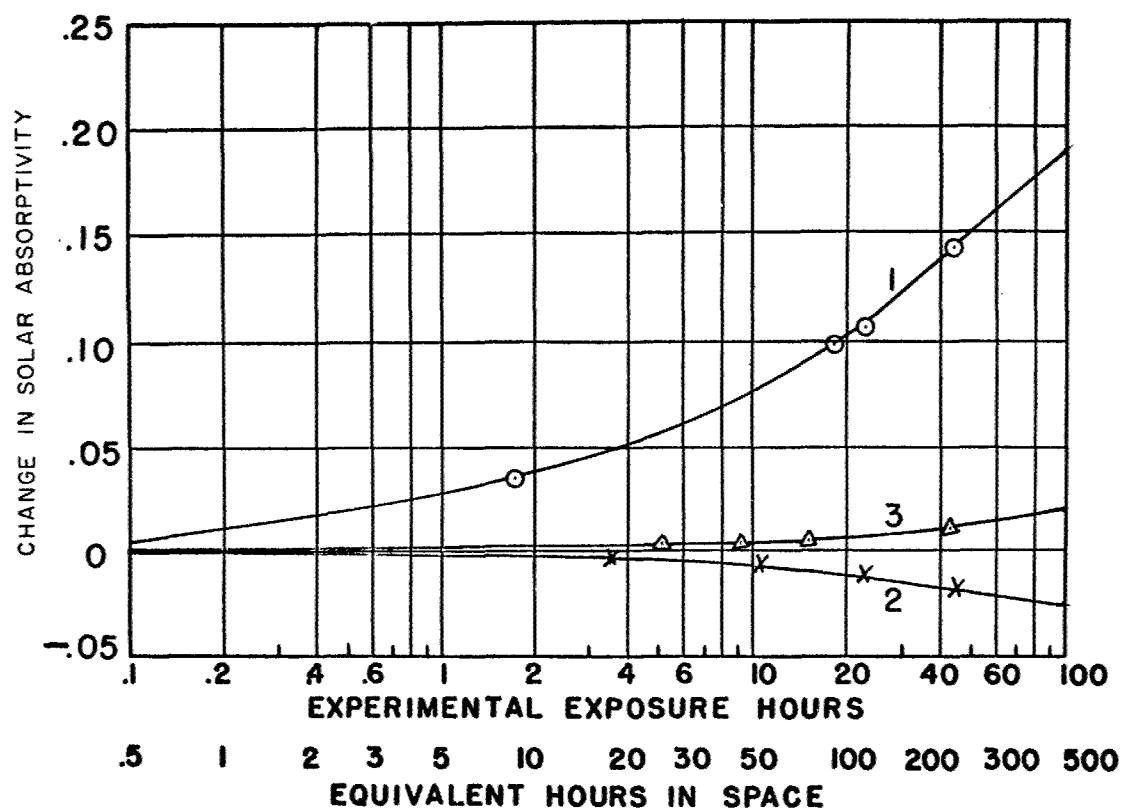


Figure 13. Photodegradation of a Silicone Alkyd.

1. Unprotected
2. Protected with 1% HBF
3. Protected with 5% HBF

After Schmitt and Hirt, Eighth Quarterly Progress Report, Contract AF 33(616)5945, January 1961

1. Dissociation and evaporation
2. Loss of adherence and shock resistance
3. Change in optical or temperature control properties
4. Diffusion

Figure 14. Effects of Space on Ceramic and Anodic Coatings

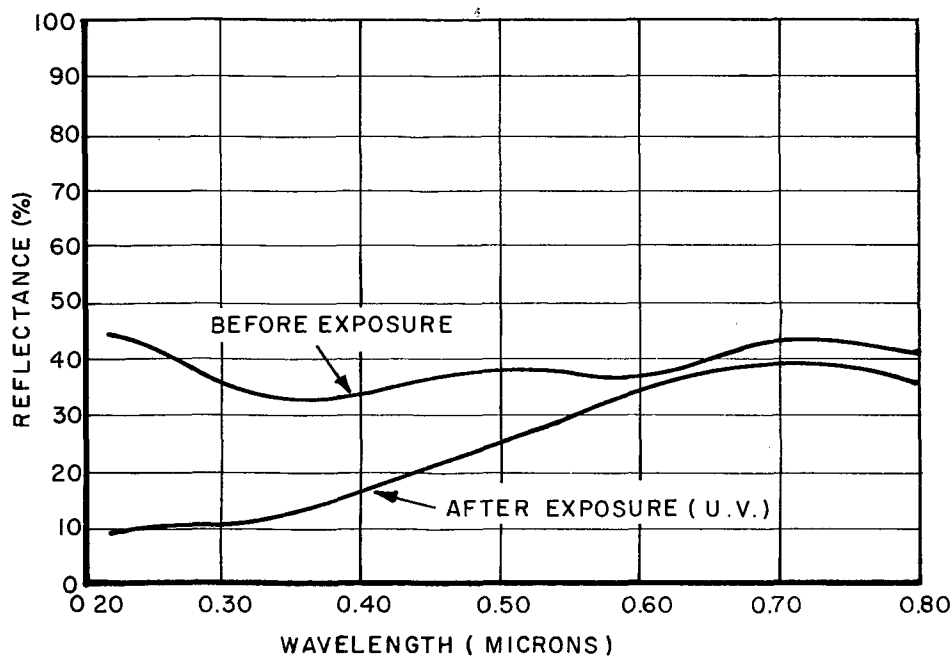


Figure 15. Change in Reflectance of Anodized Aluminum After 100 Hours of Ultraviolet Light Exposure (After Cowling, et al, WADD TR 60-773, 1960)

1. Evaporation
2. Sputtering
3. Optical Properties
 - Roughening or Smoothing
 - Vacuum Deposition
4. Physical Properties
 - Creep
 - Friction

Figure 16. The Effects of the Space Environment on Metals and Metallic Coatings

COATINGS FOR TEMPERATURE CONTROL IN SPACE VEHICLES

J. H. Weaver

Lt. Cecil Jacobs

Directorate of Materials and Processes, ASD

Introduction

In the past, coatings have been used primarily for oxidation, corrosion and erosion resistance, decoration, and in some instances to camouflage aircraft and ground support vehicles. Since the emphasis is now on space and space vehicles, these uses become secondary considerations. Coatings take on new roles as overall temperature control, to enhance the efficiency of heat sinks or radiators, for thermal insulation and for selective solar energy collection. Each of these uses are individual problems and require different coatings. This paper is primarily concerned with coatings for temperature control in space vehicles.

Figure 1 shows the thermal forces that contribute to space vehicle temperature. The space vehicle generally receives heat from several sources, but the sun is invariably the most important one. Of the minor sources of heat, internal energy always contributes to the space vehicle temperature balance. It consists of the waste energy generated in the space vehicle due to electrical resistance and mechanical friction; it exerts a minor effect on present day space vehicles but the effect will be proportionately larger in future space vehicles when more complex equipment is launched. The space vehicle receives some energy from the earth, consisting of the earth's own radiation and the solar energy reflected from the earth. The latter quantity, called albedo, is slightly richer in shorter wavelengths than is direct solar radiation. The prime source of heat, is however, absorption of solar energy by the space vehicle.

To control the amount of energy absorbed from the sun, and more important, the amount transferred to the interior of the vehicle, the design engineer must choose between conventional insulating materials and the optical properties of specifically prepared surface coatings. In all aerospace applications, weight and space factors are a prime consideration. Low thermal conductive insulating materials which reduce heat transfer to any appreciable extent are either bulky, heavy, or both as is illustrated in figure 2. Conventional insulating materials have limited utility in the problem of preventing heat transfer in space vehicle travel. However, selective coatings can reduce heat transfer while at the same time govern energy absorption adding only a small amount of weight and volume to the overall system. This may be accomplished by a brief analysis of the basic optical properties of materials. These properties may be used to prepare general types of temperature controlling systems.

Basic Optical Properties

Materials having selective optical properties can be used to control radiant heat transfer by control of the three basic optical properties: 1 reflectance, 2 absorptance and 3 emittance. In most practical systems, a balance between these three conditions will be used to obtain the desired temperatures as illustrated in figure 3.

Energy incident upon an opaque space vehicle surface will be reflected or absorbed. If it is reflected, the energy is diverted and will not cause a rise in temperature. However, if the energy is absorbed, it must be reradiated. The reradiation of the absorbed heat is independent of its source, but at equilibrium, it must be numerically equal to the absorbed energy. The temperature required to radiate the absorbed heat is dependent upon the emittance of the exterior surface and the exposed area of the space vehicle. Since the geometry factors are fixed on a given space vehicle, the temperature is now a function of the ratio of the absorption coefficient and the emittance.

This can be better understood by referring to figure 4. The solar energy is at short wavelengths and a coating which is dark in the visible and near infrared will absorb much of the sun's energy. At equilibrium, all the absorbed energy is reradiated at wavelengths represented by the right curve. Since the reradiation is at longer wavelengths, the power of a coating to radiate heat often differs from its power to absorb heat. This is shown in figure 5. The white coating absorbs very weakly, but is a very efficient radiator of heat, that is, it has high emittance which provides a very cold surface.

The complexity of controlling the heat balance is made more difficult by orbital and space environmental factors, but it has been shown that all of these problems can be overcome through the application of scientific principles. The varying degree of success attained with space probes and orbiting vehicles, has revealed both the existence of the temperature control problem as well as a logical approach to its solution.

A payload, heated by solar radiation on the one hand and cooled by reradiation on the other, must be protected from widely varying temperature differentials. Constant temperatures are presently maintained by techniques such as painting, polishing and shuttering. Ultimately, a material is sought which has the proper conditions to obtain the required optical properties.

Metallic Coatings

A number of different types of inorganic and organic coatings have been used successfully in designing specific heat balances within the various spacecrafts which have been launched to date. A spherical body which absorbs and reradiates heat with the same efficiency ($\alpha = \epsilon = .5$) will operate at approximately 40°F, neglecting the earth's heat contribution. This condition is approximated by a flat black organic coating. Metallic coatings generally absorb little solar energy, but absorb infrared energy even to a lesser extent. This is shown in figure 6. Aluminum, for instance, absorbs 12 percent of the sun's energy but has an emittance of 3 percent. The result is a very high temperature of about 250° - 300°F, again neglecting the earth's heat contribution. Similar effects are observed with other metals such as stainless steel. For this reason, almost all metal coatings have high solar α/ϵ ratios. Therefore, an uncoated metal sphere would give us a hot space vehicle. The temperature of the metallic coating can be reduced in a number of ways. If the metal surface is sandblasted, the infrared reflectance is reduced more rapidly than the short wavelength reflectance, thus decreasing the solar α/ϵ ratio. It can be coated with a material which is transparent to solar energy but black or emissive in the infrared. This is true of many lacquers and inorganic coatings such as silica. Inorganic or organic coatings, for example, alumina or a white enamel respectively, can be applied in stripes or over the entire metal surface to increase the emittance with or without affecting the solar absorption. Metals can be combined with organic coatings to get a compromise in properties. Thus an aluminized silicone, has an absorption of 40 percent and an emittance equal to about 0.3 or an α/ϵ ratio of 1.3. By changing the solar α/ϵ ratio of the metal coatings, one can control the temperature.

One method of temperature control of an electronic blackbox in a heat radiation field is to place it in a container whose surface has known optical properties. The fabrication of a container entirely of a material of known and desired optical properties, such as gold or silver, is impractical because of weight, economy, mechanical strength, and cost of mechanically polishing the surface. Therefore, the outside of the blackbox could be coated with a material containing the desired optical properties, again saving some of the overall weight and space problem. Gold, silver, copper and aluminum are being used on metallic and nonmetallic substrates to produce highly reflective surfaces to heat radiation as shown in figure 7.

Organic Coatings

Organic coatings are virtually all very absorptive in the infrared and hence have high emittance. Such a surface is the most stable and efficient to use for long heating periods. The short wavelength absorption can be readily varied by pigmentation with organic and inorganic materials. The organic coatings will have α/ϵ ratios of 1 or less and can be used to give cool or cold surfaces in space (figure 8). It is obvious that the reflectance and the absorptance of the pigmented coating varies with the pigment. A leafing aluminum pigment is the most efficient reflector of ultraviolet energy. Several white pigments are superior to leafing aluminum in the visible and near infrared spectral regions, but are inferior to it as a reflector of ultraviolet energy. Of the nonleafing pigments, basic white lead carbonate is superior to all others in reflecting ultraviolet energy. The white lead pigmented coatings lose much of their efficiency as ultraviolet reflectors when exposed to the simulated space environment. In other regions of the spectrum, zinc sulfide is an excellent reflector of visible and near infrared energy. Other paint formulations using rutile, carbon black, red iron oxide and chrome oxide green in various amounts are used as the pigments, depending on the ratio desired.

Inorganic Coatings

Inorganic (anodic and ceramic) coatings are generally quite absorptive in the infrared although their absorption is less than most organic coatings. Many of the inorganic materials used as pigments in an organic binder give a high reflectance to difference in refractive index between the pigment and binder. However, emittance of 0.4 to 0.85 for the bulk material is common. Ceramic coatings may be used to give cool surfaces, but at present these coatings are most effective in increasing the reflectance when used as a pigment in organic coatings.

Ceramic coatings are somewhat inferior to organic coatings when α/ϵ ratios, application ease, and mechanical properties are considered. The one main advantage ceramic materials have over organic materials is their thermal stability. For example, flame sprayed aluminum oxide, having an emittance up to 0.85, has utility at temperatures many times that of the pigmented organic. The coating, however, is brittle and unable to stand rigorous thermal shock.

One important role ceramics plays in temperature control is that of diffusion barriers for highly reflective (low emittance) coatings. The temperature stability of ceramics combined with their chemical structure can be controlled to suitably deter diffusion, and consequently contamination of the reflective metal. Materials such as SiO, NiO, CeO, and NBS ceramic A-418 have prevented diffusion between gold and Inconel-X at 1500°F for periods up to 300 hours.

Some evaluation has been made on methods to improve the emittance of anodized coatings. By taking advantage of the porous coating, a high temperature dye or other pigments may be sealed within the coating to increase its emittance. Some work is being done with anodized coatings to provide a surface with a ratio of solar absorptance to long wavelength emittance of less than 0.2. Pure aluminum oxide is considered transparent to radiation in the visible region. Therefore, polished aluminum with a transparent coating of aluminum oxide would be expected to possess a low α/ϵ ratio. This is a double surface effect since the polished aluminum reflects the solar radiation which is permitted to penetrate the aluminum oxide coating.

Problem Areas

Because of their unique functions, coatings used for temperature control introduce many problem areas. The old problems of oxidation, diffusion, cleaning and application techniques will be supplemented by the influence of the space environment. (These problem areas are shown in figure 9.)

The coating materials presented must withstand the space environment and in particular, ultraviolet radiation, vacuum, and temperature extremes. These particular problems will be discussed in length in the accompanying paper on environmental considerations.

One of the problem areas in the use of reflective metal surfaces is oxidation. When a metal oxidizes it will change the reflectance properties of the metal. For example, clean polished copper has a reflectance of 0.97 to 0.98 in the temperature range 600° to 1800°F, whereas oxidized copper has a reflectance of 0.75 to 0.85 in the same temperature range. This means that any metal to be useful as a highly reflective coating against heat transfer must be oxidation resistant or must be protected from oxidation. At present, few materials are known which can both protect a metal from oxidation at elevated temperatures and are sufficiently transparent to radiant energy. The requirement of oxidation resistance without an overcoat eliminated as high temperature reflective coatings the use of all metals except gold, rhodium and platinum. Much effort is being directed toward the development of oxidation resistant coatings which will not reduce the reflectivity of metal surfaces. When it appears, oxidation resistance cannot be built into the basic metal, effort will have to be extended toward finding a suitable transparent overcoat.

The major problem associated with the use of a reflective metal such as gold as a high temperature-high reflectance coating is that it readily diffuses with practically all substrate materials at temperatures above 600°F. This diffusion is a very serious problem and a major effort in research is needed to obtain methods of retarding the diffusion with substrate materials.

Another serious problem area associated with selective coatings for temperature control is the application techniques necessary to produce high quality coatings. Trace amounts of extraneous materials may significantly influence the optical properties of the coatings. Materials, such as sensitizers and activators, may influence the resistance of the coating to the deterioration of the optical properties because of radiation or vacuum effects. From all indications, problems of contamination control are going to become more critical in the future. Advances in the state-of-the-art in cleaning and application techniques are necessary to make significant advances in temperature control coatings.

Summary

It has been shown that radiant heat transfer in space can be effectively controlled with coatings having selective optical properties. Since these coatings must be designed for a special system and cannot be altered after the launch of that system, research and development must continually be in advance of present needs. It must produce methods whereby special optical properties can be built into organic, inorganic and metallic materials. These methods of building are not presently available. Only token effort has been expended to understand the mechanisms controlling selective optical properties. Only through vigorous and imaginative research and development programs can we obtain these answers. Research and development must present methods for the control of other problems such as ultraviolet light breakdown, higher thermal stability, better application techniques and better evaluation procedures.

In conclusion, the Air Force fully intends to continue the pursuit of vigorous programs of materials research and development in temperature control of space vehicles. As the speeds and complexity of aerospace vehicles become greater, the need for temperature control will increase. The conquest of space is a huge undertaking and requires the utmost in a cooperative effort encompassing not only the military services and other Government agencies, but all of industry and academic centers as well. A unified, coordinated, cooperative effort with all elements contributing creative thinking, time, and resources to best advantage cannot be overstressed if we are to attain our goals.

BIBLIOGRAPHY

1. Belser, R. B., et. al., "Reflective Inorganic Coatings," ASD TR 61-151, 1961
2. Harrison, W. N., et. al., "Standardization of Thermal Emittance Measurements," WADC TR 59-510, 1960
3. Schmit, R. C., et. al., "Studies on the Protective Ultraviolet Absorbers in a High Vacuum Environment," WADC TR 59-354, 1960
4. Withers, J. C., et. al., "Development of Heat Barrier Coatings," ASD TR 61-5, 1961
5. Van Vliet, R. M., "Spectrally Selective Coatings for Temperature Control of Space Probes," WADD TR 60-386, 1960
6. Van Vliet, R. M., "Organic Coatings for Control of Spacecraft Temperatures," ASD TN 61-72, 1961
7. Proceedings - "Coatings for the Aerospace Environment," WADD TR 60-773

SPACE VEHICLE ENERGY BALANCE

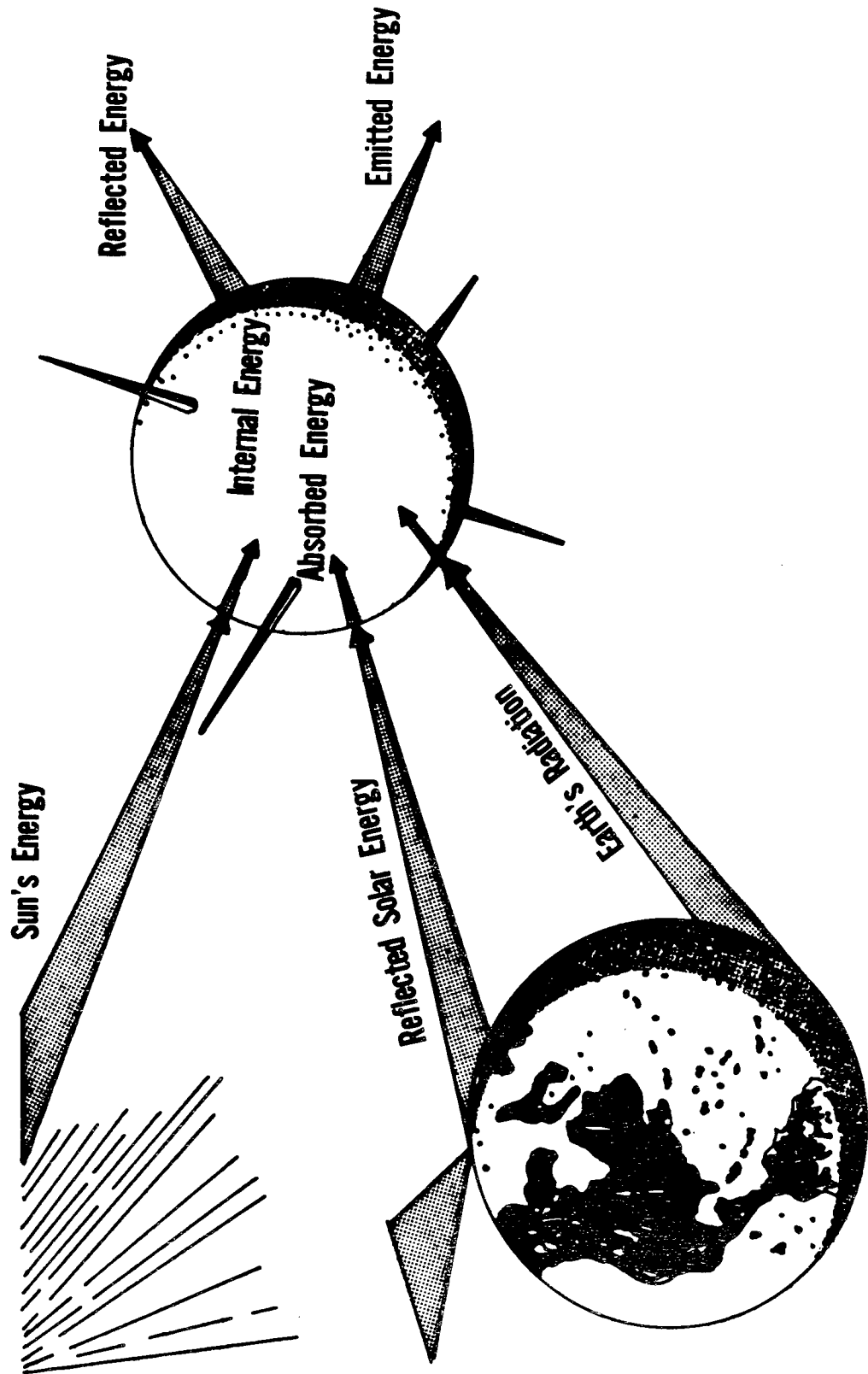


Figure 1.

THIN FILMS VS. HEAVY INSULATING MATERIAL

24" DIAMETER SPHERE

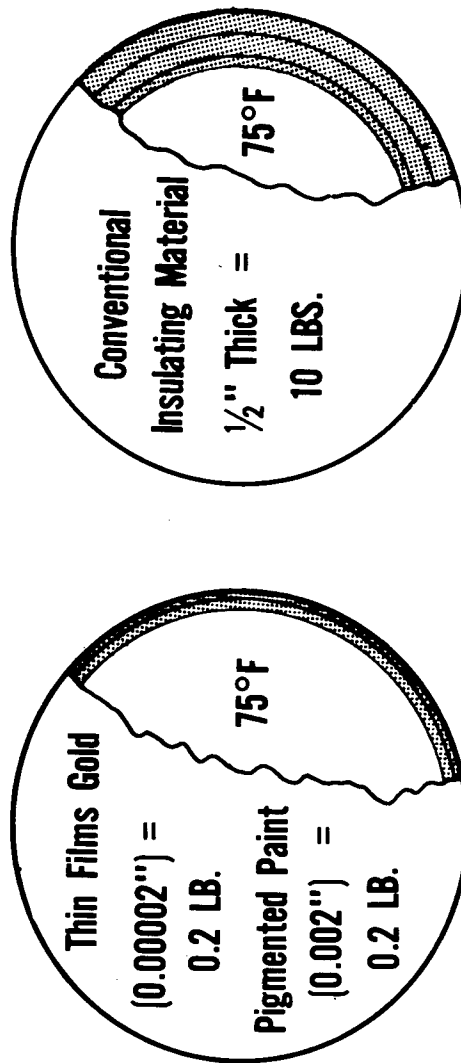


Figure 2.

COATING	SOLAR			TEMPERATURE °F	
	REFLECTION	ABSORPTION	EMITTANCE	SPHERE	STRIPED SPHERE
WHITE	0.82	0.18	0.95	-135	-20
WHITE PLUS CARBON BLACK	0.47	0.53	0.95	-30	32
FLAT BLACK	0.03	0.97	0.95	45	85
FLAT BLACK PLUS ALUMINUM	0.05	0.95	0.80	65	120

Figure 3. Vehicle Temperature Control

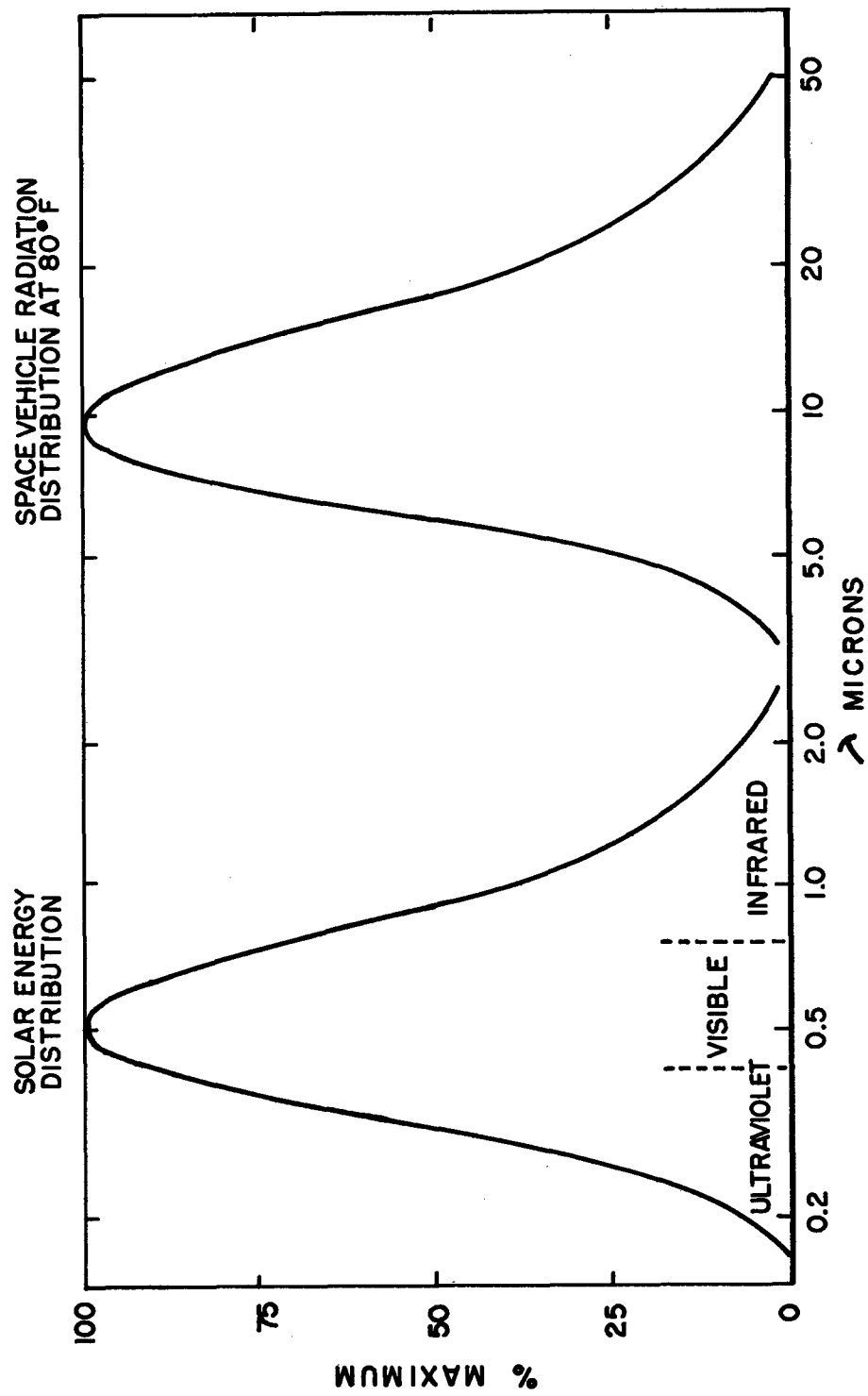


Figure 4. Relative Spectral Distribution of Heat from Sun and Space Vehicle

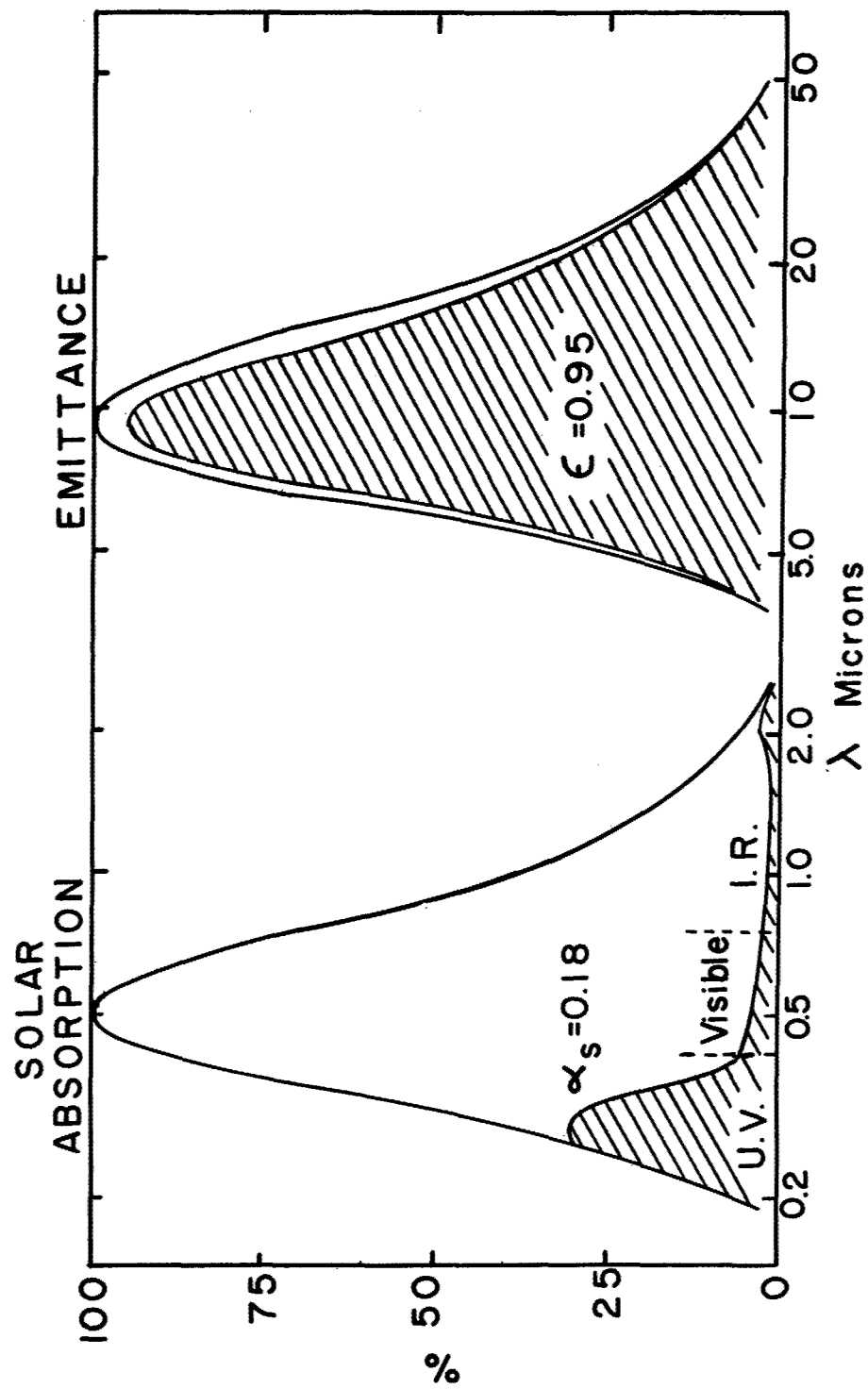


Figure 5. A Graphical Representation of a White Organic Coating Designed for Maximum Cooling

COATING	α / ϵ	TEMPERATURE °F
ALUMINUM	4.0	250
STAINLESS STEEL	2.5	170
ALUMINIZED SILICONE	1.3	60
ALUMINUM + CLEAR LACQUER	1.0	40
WHITE ORGANIC PAINT	0.2	125

Figure 6. Equilibrium Temperature of Spherical Space Probes with Various Coatings

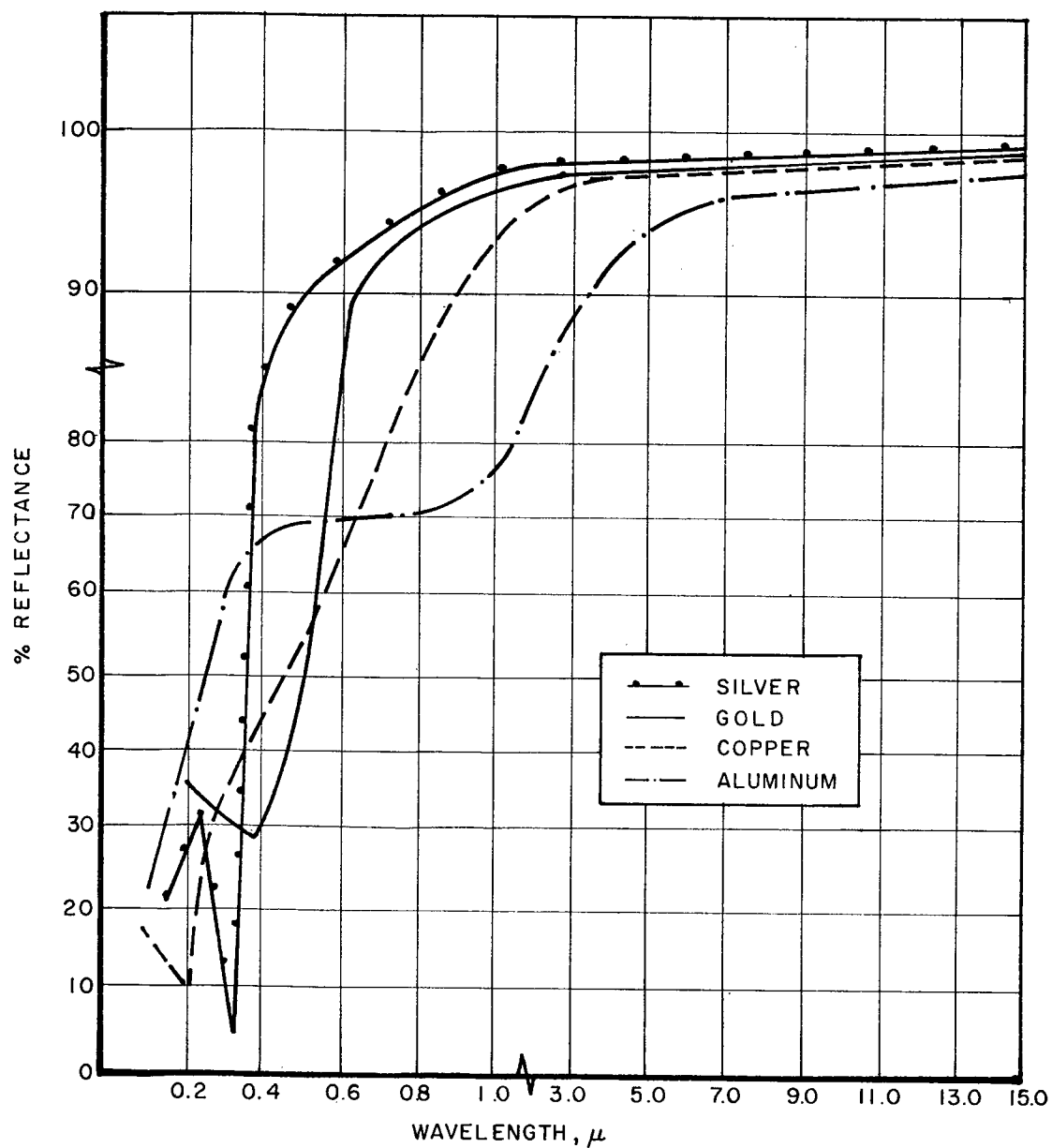


Figure 7. Metallic Surfaces

<u>ORGANIC MATERIAL</u>	<u>α</u>	<u>ϵ</u>	<u>α/ϵ RATIO</u>
White (30 % PV Zinc Sulfide) Silicone	0.31	0.77	0.40
Grey Silicone	0.53	0.95	0.55
Leafing Aluminum in Silicone	0.32	0.33	0.98
White Lead Carbonate (30 % PV) Silicone	0.46	0.46	1.0
Dull Black (Vinyl Phenolic)	0.93	0.84	1.1

Figure 8. Organic Material Radiative Properties

PROBLEM AREAS, SUMMARY

Evaporation

Vacuum

Temperature Stability

UltraViolet Radiation

Oxidation

Diffusion

Cleaning Techniques

Application Techniques

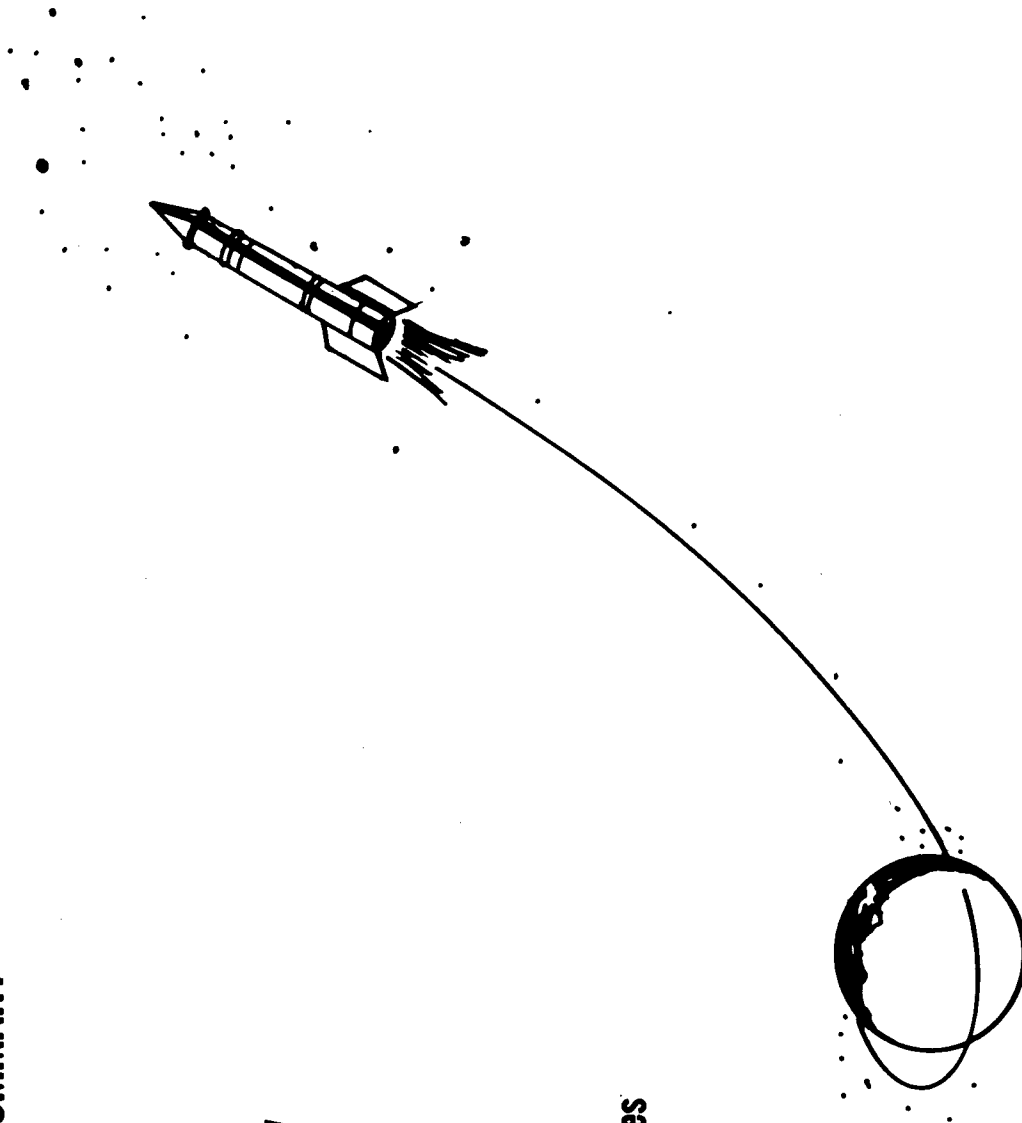


Figure 9.

THERMAL PROTECTION

H. Marcus

Directorate of Materials and Processes, ASD

Recent advances in space technology have necessitated consideration of a large number of hypervelocity vehicles which are expected to operate over a wide band of flight conditions. Each of these vehicles requires thermal protection to withstand the environments created by the flight trajectories. We shall endeavor to describe several passive thermal protection systems, with the aid of tables and figures, and to provide some guidance for fruitful areas of investigation. We shall also present a method for the judicious selection of a particular protection phenomenon for a specific application.

The selection of a thermal protection system becomes particularly important for those mission profiles which expose structures to relatively low heat transfer rates for long time periods and those which couple low heat rates with intermittent high heat transfer rates typical of controlled re-entry.

If all the heat acquired by the material were retained, the material might undergo changes which would impair or destroy its usefulness. However, there are many ways by which the material can utilize, dissipate, or be shielded from the heat. These modes of transference and protection are listed in table 1.

Heat may be transferred from an environment to a material by (a) convection — the transportation and exchange of heat by moving masses of matter (usually a liquid or a gas) in the vicinity of the material (b) conduction — the exchange of heat through matter in direct contact with the material (c) radiation — the exchange of heat between the material and some other body of material or mass of hot gas not in direct contact, where the energy is transmitted through the intervening medium in the form of electromagnetic waves without warming of the medium; and (d) chemical heating — heat resulting from exothermic chemical reactions within, on, or adjacent to the surface of the material.

The material may be protected from acquiring excessive heat by the following methods:

1. **Sensible Heating (heat storage):** Retention of heat by the material, resulting in an increase in its temperature.
2. **Change of Phase:** The transfer of heat resulting from a change in the material from one phase to another. There is a specific amount of heat which must be transferred to produce each change of phase. For example, when a material changes from a solid to a liquid, a quantity of heat called the latent heat of fusion must have been transferred to the material.
3. **Liquid Film:** The liquid phase of a material which forms on the surface and reduces the heat which is transferred to the material by increasing its own sensible heat. The behavior of the liquid film (in contrast to the solid phase) involves fluid mechanics in addition to simple heat storage.
4. **Mass Transfer Cooling:** A highly effective shielding mechanism which may result from the ejection of gases from the material's surface. The gases reduce the convection rate to the solid surface by reducing the temperature and velocity gradients in the fluid

boundary layer adjacent to the material's surface and by acting as a thermal sink in the boundary layer. Some mass transfer cooling is achieved by surface liquid formation transport.

5. Magnetohydrodynamic Effects: The effect of a magnetic field upon an ionized fluid stream adjacent to a material. The magnetic field deflects the fluid from its normal path, reducing the heat transfer by thickening the boundary layer and consequently reducing the velocity and temperature gradients adjacent to the surface.

6. Thermoelectric Effects: Heat transfer between two materials by means of an electric current through a junction of dissimilar metals or by electron emission. The junction phenomenon is known as the Peltier effect, and can be used with an external power source to construct a refrigeration machine consisting of an electrical circuit, without moving parts, which absorbs heat at one junction and rejects it at the other. In the use of other phenomena, electrons emitted from a hot source, as in the cathode of a vacuum tube, are carried away and deposited in the cooler region, which is connected electrically to the hotter region, completing the circuit and replenishing the cathode with electrons and redistributing the heat over a larger region. Both of these methods are reversible under certain conditions.

The basic heat balance relationship is predicated on the axiomatic principle that the total of the heat supplied must be equal to the total of the heat utilized, shielded, and dissipated (the radiated and chemical heat terms may be combined as single net terms) as indicated in table 2.

Since the major emphasis has been placed on those systems which provide passive protection, that is, radiation, heat storage, and mass transfer cooling, my remarks will be directed along these lines. We are not going to be concerned with ablation at this time since the subject of mass transfer cooling by ablation is covered by another panel. These three phenomena display entirely different thermal protection characteristics and these are summarized in table 3 with regard to heat flux rates, heat fluxes, and heat absorbed per unit weight. These three characteristics are the primary features of a given thermal environment and protection problem.

The only limitation on the use of thermal radiation as a protective phenomenon is in the rate at which heat can be emitted. This limitation is dependent upon maximum allowable material surface temperatures and, to a lesser extent, on surface emissivity. Radiation cooling is independent of the duration of heat flux and is not directly associated with any weight penalty.

The characteristics of heat storage as a protective phenomenon are intimately related to the transient behavior of materials exposed to heating. Analysis of a simple representative problem, wherein a material is subjected to a constant one-dimensional heat flux rate, q , at an exposed surface for a period of time, t , shows that there is a maximum value of the parameter $q\sqrt{t}$ which may be employed for nondestructive use of the material. The value of this parameter is directly related to maximum allowable material surface temperature and, to a lesser extent, upon thermal conductivity. Since the parameter $q\sqrt{t}$ is limited, both the heat flux rates and heat fluxes in a given application problem must be considered simultaneously. Heat storage functions as a protection phenomenon through stored sensible heat in the material; therefore, the heat absorbed per unit weight is limited by the permissible temperature rise and specific heat of the material.

Mass transfer cooling operates as a protection phenomenon against convective heat inputs. In high speed flight applications, the phenomenon is utilized most efficiently if the mass transfer coolant is in the gaseous phase throughout the boundary layer adjacent to the surface of the flight vehicle. Under these conditions, the effective heat absorbed per unit weight by the mass transfer coolant is directly proportional to the enthalpy or temperature difference causing heat transfer as well as being inversely related to the molecular weight of the coolant. Hence, the effective heat absorbed per unit weight depends upon both the environmental and coolant characteristics. At present there seems to be no known limitations on the use of this phenomenon with respect to heat flux rates or heat fluxes present in a particular application problem.

The characteristics of the thermal protection phenomena discussed above are quantitatively depicted in figure 1. The two coordinates employed represent the thermal environment. The abscissa corresponds to the heat flux rate and the ordinate represents the heat flux, which is the time integral of the heat flux rate and therefore represents the total heat input per unit area.

The vertical lines shown in figure 1 pertain to the use of radiation cooling as a protective phenomenon. Each vertical line represents constant values for the heat flux rate emitted from the surface of a material. Along each line is indicated the corresponding value of the product of the absolute surface temperature, T_w , and the fourth root of surface emissivity, ϵ , as determined from the Stefan-Boltzmann law applied to gray surfaces. For a given heat flux rate and surface emissivity, the corresponding surface temperature requirement can consequently be determined from the appropriate vertical line. Since the lines are vertical, it is apparent that this form of thermal protection is not dependent on heat flux, Q , or material weight.

Two sets of lines pertaining to the use of heat storage appear in figure 1. The diagonal lines correspond to constant values of the parameter $q\sqrt{t}$ (where q is a constant heat flux rate). The horizontal lines denoted by ϕH_{av} correspond to the total heat flux, Q , which is the sensible heat stored. The quantity ϕ represents the weight per unit surface area of the heat-absorbing element, and the quantity H_{av} represents the average heat stored in this element per unit weight. The use of heat storage as a protective phenomenon may therefore be dictated by either material limitations, as represented by the diagonal lines, or by weight limitations, as represented by the horizontal lines.

The horizontal lines in figure 1 denoted by the symbol κH_{eff} are related to the use of mass transfer cooling. Each of these lines corresponds to a particular value of the total heat flux as determined for heat transfer in the absence of mass transfer action and at the same surface temperatures. A similar qualification applies to interpretation of the heat flux rate coordinate in this case. The quantity κ represents the weight injected (or ablated) per unit surface area, and the quantity H_{eff} represents the effective heat of ablation of the mass transfer coolant employed. For a given situation, with known thermal environmental conditions and a particular coolant, the quantity H_{eff} can be evaluated. The horizontal lines would then permit determination of coolant weight requirements.

The thermal environment existing in a given application can be represented by a region. The characteristic regions associated with several severe thermal environments are depicted in figure 2. The information contained in this figure relative to both the thermal environments and the modes of thermal protection aids in delineating those modes which may be most advantageously employed in a given environment. For example, consider the ballistic missile thermal environment. A cursory examination of the vertical lines passing through this region shows that over much of this region, surface temperature

requirements are prohibitive for consideration of radiation as a primary means of thermal protection. This leads to examination of relative merits of heat storage and mass transfer. For known heat storage materials applicable for flight vehicles, the most promising have maximum values of the q/\sqrt{t} parameter of less than 4000 Btu/ft²/sec^{1/2} with an associated H_{qv} of approximately 1000 Btu/lb. However, mass transfer coolants in this application might realize values of H_{eff} between 4000 and 12,000 Btu/lb for laminar flow conditions at the flight velocities associated with the aerodynamic heating. Correlation of the above information with the ballistic missile thermal environment shows that:

- a. Heat storage protection is not adequate over a major portion of the environmental region because of excessive requirements for the q/\sqrt{t} parameter.
- b. In those portions of the environmental region where heat storage protection is feasible, a comparison of H_{qv} of the heat storage material with H_{eff} for mass transfer coolants shows that the mass transfer cooling system would afford a significant weight-saving possibility. On this basis, the most promising primary thermal protection phenomenon for use on ballistic missiles is mass transfer cooling. In addition, if materials are used which form high temperature surfaces during re-entry, radiation cooling can be an important secondary form of thermal protection which does not introduce any penalty in the form of weight.

The preceding discussion demonstrates that the process of selecting a suitable form of thermal protection involves several steps. The results of this step-by-step procedure, for other thermal environments depicted in figure 2 as well as for the ballistic missile case, are schematically represented in table 4. Some of the salient factors in arriving at the results indicated for the other thermal environments are briefly discussed.

For the glide vehicle thermal environment, the feasibility of employment of radiation cooling is improved over that existing in the ballistic missile environment because of the lower heat flux rates with attendant lower surface temperature requirements. Furthermore, the expected heat inputs per unit area preclude primary dependence upon either heat storage or mass transfer cooling systems because the associated weights would be prohibitive on a flight vehicle. Consequently, radiation is the most suitable primary protection phenomenon in this application. For secondary protection at local hot spots, mass transfer cooling would provide a weight-saving advantage over a heat storage system, since the values of the effective heat of ablation of the mass transfer coolant, H_{eff} , and the average heat stored per unit weight of heat storage material, H_{qv} , are similar to those encountered in the ballistic missile application. Consideration of the effect of changes in geometry on vehicle flight performance might require that the mass transfer cooling system be of a gas-injection rather than an ablation type.

The region indicated for thermal radiation from nuclear explosions corresponds to nonattenuated radiation from explosions in the 100 to 200 kiloton yield range at distances down to 2000 feet from the explosion. For these selected conditions, total heat fluxes resulting from the explosions do not appear to be a serious problem for either the glide vehicle or the ballistic missile. However, the peak heat flux rates from such an explosion may be significant enough to cause local overheating if glide vehicles were constructed with thin-skinned surfaces lacking heat storage capabilities. The mass transfer phenomenon is not applicable to protect against radiative heat inputs of this type. Thermal damage could be avoided by providing additional sufficient heat storage capacity in the skin. Reradiation following the input from the nuclear explosion could be used as a secondary protection to re-establish equilibrium conditions.

The thermal environment in a rocket motor constitutes a unique thermal protection problem. Turbulent flow conditions prevail, and the geometry of the nozzle must be preserved within prescribed limits during operation. Because of the internal cylindrical geometry, radiation protection at the critical nozzle throat region is not applicable. The combination of turbulent flow conditions and temperature differences across the boundary layer, which are significantly lower than in the external environment of hypersonic flight, tend to markedly reduce the effectiveness of mass transfer cooling. Simultaneous consideration of geometry requirements and the limited effectiveness of the mass transfer cooling phenomenon under the prevailing conditions appears to preclude the direct application of an ablation form of mass transfer cooling, at least in the critical throat region. A gas injection form of mass transfer cooling may still be a promising system. Conventional modes of protection have utilized heat storage or, in some liquid-fueled rockets, heat transfer through the nozzle wall to a flowing fluid coolant.

There are other passive protective phenomenon which were not touched upon because of time considerations. The subjects of radiation heat shields and thermal insulations have not been discussed for the same reason. We recognize these as potential systems as well as some of the absorptive variety such as convective cooling and transpiration cooling. Transpiration cooling has received considerably more attention than convective cooling since it is a form of mass transfer cooling, and because of the inherent problems associated with circulating cooling systems of the liquid metal variety. This is not to say that transpiration cooling is free of problems. The most difficult problem peculiar to this system is the fabrication and maintenance of porous surfaces.

The current state of the art for thermal protection systems leaves a great deal to be desired. The capabilities we possess today are relative only to first generation developments which are considerably removed from the anticipated goals with respect to efficiency and reliability. It is clearly evident that the heat storage system is inherently limited to short time exposures of five minutes or less because of heat penetration and structural decomposition. Perhaps increased consideration is indicated here for absorptive systems based on liquid cooling for long-time applications, with development of reliable, lightweight pumping systems. The need for increased R & D activities in the development of radiation cooled systems is evident for advanced glide re-entry vehicles subject to high radiative equilibrium temperatures and high cumulative heat input characteristics. Radiative heat shield systems would bear further investigation in this system. The solid propellant rocket nozzle presents a serious challenge to thermal protection. It is conceivable that a solution may be found in an unusual combination of several thermal protection systems. This is not the end; only the beginning.

BIBLIOGRAPHY

1. Allen, H. J., and Eggers, A. J., Jr., A Study of the Motion and Aerodynamic Heating of Missiles Entering the Earth's Atmosphere at High Supersonic Speeds, NACA TN 4047, October 1957.
2. Glasstone, Samuel, Editor, The Effects of Nuclear Weapons, USAEC, June 1957.
3. van Driest, E. R., The Problem of Aerodynamic Heating, Aero. Eng. Review, Vol 15, No. 10, October 1956, pp. 26-41.
4. Sziklas, E. A., and Banas, C. M., Mass-Transfer Cooling in Compressible Laminar Flow, Presented at Symposium on Mass Transfer Cooling for Hypersonic Flight Vehicles, June 24, 1957.
5. Bonin, J. H., Price, C. F., and Taylor, D. E., Determination of Factors Governing Selection and Application of Materials for Ablation Cooling of Hypervelocity Vehicles, WADC TR 59-87, July 1959.
6. Manos, W. P., Taylor, D. E., and Tuzzolino, A. J., Thermal Protection of Structural, Propulsion, and Temperature-Sensitive Materials for Hypersonic and Space Flight, WADC TR 59-366, July 1960.

Table 1

MODES of HEAT TRANSFER and MATERIAL PROTECTION

HEAT MAY BE TRANSFERRED FROM AN ENVIRONMENT TO A MATERIAL BY:	THE MATERIAL MAY BE PROTECTED FROM ACQUIRING EXCESSIVE HEAT BY:
Convection	Sensible Heating
Conduction	Change Of Phase
Radiation	Reradiation
Chemical Heating	Chemical Cooling
	Liquid Film Formation
	Mass Transfer Cooling
	MHD Effects
	Thermoelectric Effects

Table 2

BASIC HEAT BALANCE RELATIONSHIP

	HEAT (Sensible)
	+ HEAT (Phase Change)
HEAT (Convected)	+ HEAT (Liquid Film)
+ HEAT (Conducted)	+ HEAT (Mass Transfer)
+ HEAT (Net Radiated)	+ HEAT (MHD)
+ HEAT (Net Chemical)	+ HEAT (Thermoelectric)
TOTAL HEAT (Supplied)	= TOTAL HEAT (Utilized + Dissipated + Shielded)

Table 3

CHARACTERISTICS of THERMAL PROTECTION PHENOMENA

Thermal Protection Phenomena	Permissible	Permissible	Permissible
	Heat Flux Rates BTU/FT ² -Sec	Heat Fluxes BTU/FT ²	Heat Absorbed Per Unit Weight, BTU/LB
Radiation	Limited By Maximum	No Limitations	No Limitations
	Material Surface Temperatures		
Heat Storage	Limited By Material Surface Temperatures And Thermal Conductivity	No Limitations	Limited By Maximum
			Material Temperature Rise And Specific Heat
Mass Transfer	No Limitations	No Limitations	Limited By Combination of Environmental And Coolant Characteristics

Table 4

RELATIVE COMPARISON OF MODES OF THERMAL PROTECTION IN SELECTED THERMAL ENVIRONMENTS

THERMAL PROTECTION PHENOMENON THERMAL ENVIRONMENT	HEAT FLUX RATES ENCOUNTERED (BTU/FT ² - SEC)			HEAT FLUXES ENCOUNTERED (BTU/FT ²)			WEIGHT OF THERMAL PROTECTION SYSTEM REQUIRED (LB/FT ²)			OVER-ALL RATING					
	Radiation	Heat Storage	Mass Transfer	Radiation	Heat Storage	Mass Transfer	Radiation	Heat Storage	Mass Transfer	PRIMARY PROTECTIVE PHENOMENON	SECONDARY PROTECTIVE PHENOMENON				
Hypersonic Flight Applications															
Ballistic Missile															
Glide Vehicle															
Rocket Motor Nozzle															
Thermal Radiation															
From Nuclear Explosions (On Flight Vehicles)															

Relative Ratings of Protection Phenomena for Selected Application Characteristic

Excellent

Good

Fair

Poor

Protection Phenomenon Not
Applicable to Thermal Environment

Primary Protection Phenomenon Used for Basis
of Secondary Phenomenon Selection

THERMAL RADIATION HEAT FLUX AS A FUNCTION OF SURFACE TEMPERATURE & EMISSIVITY

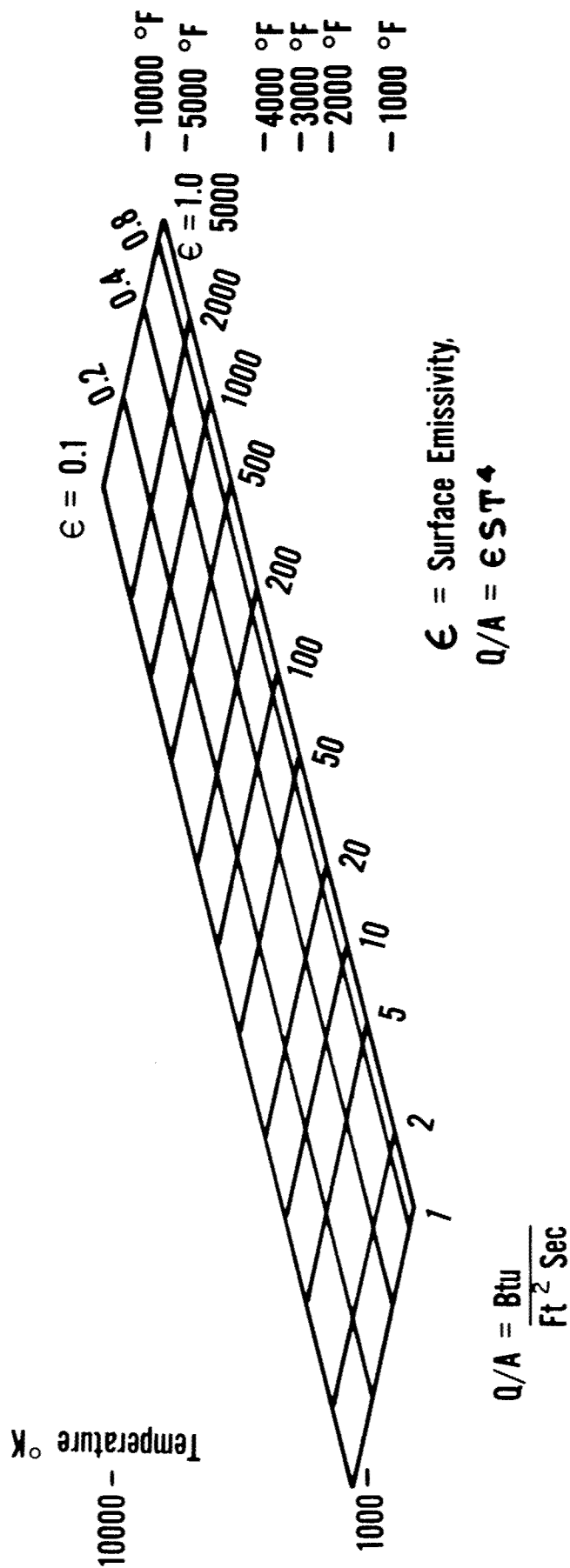


Figure 1.

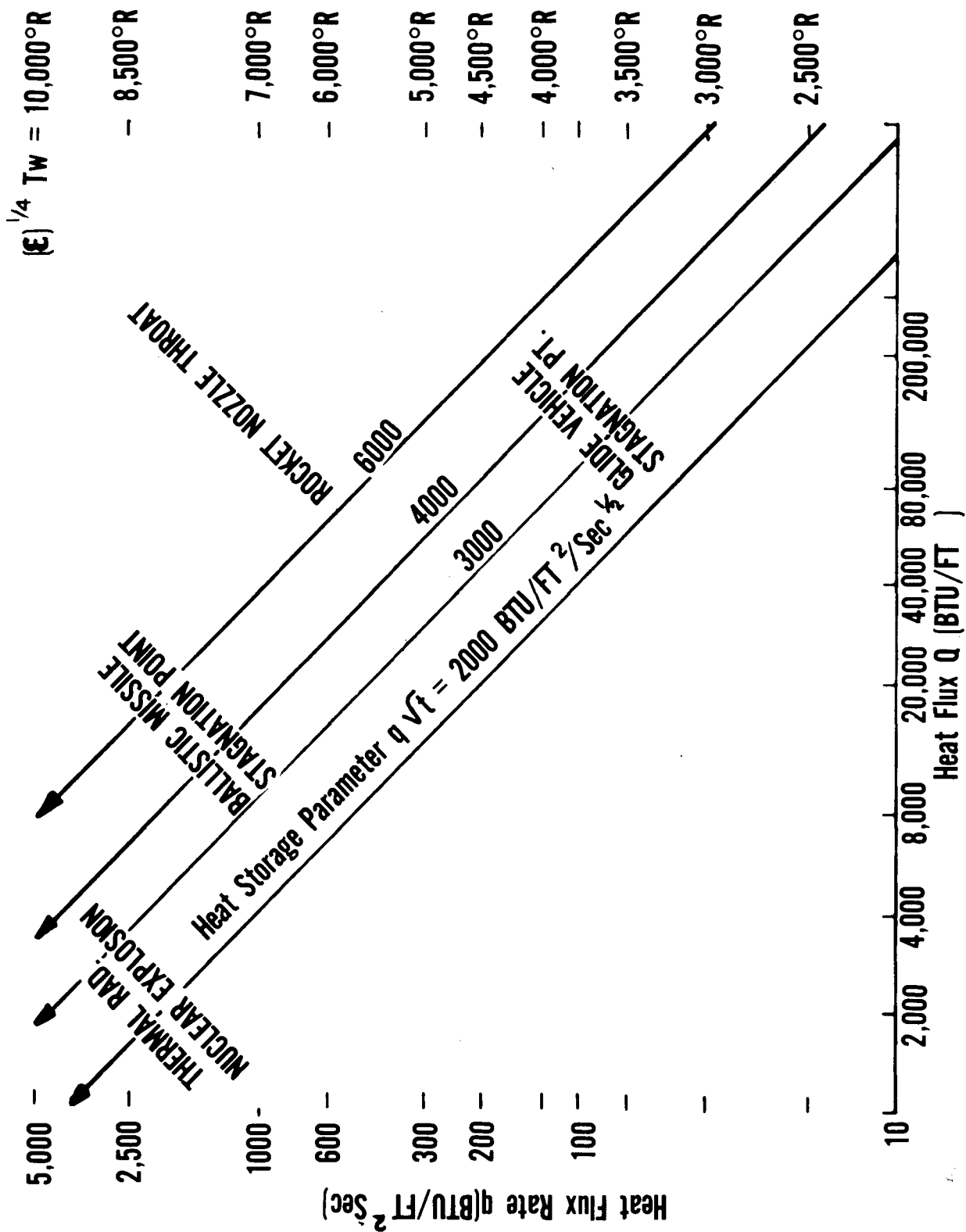


Figure 2. Comparison of Thermal Environments and Modes of Thermal Protection

REFRACTORY EMISSIVE COATINGS

L. N. Hjelm, Lt. USAF

Directorate of Materials and Processes, ASD

Introduction

The current interests in high temperature applications involving vehicle structures for long time or repeated use at high temperatures in air has spurred considerable activity in the field of refractory coatings. Radiation cooling as a thermal protection technique came to the forefront with the development of glide re-entry vehicle concepts. It is here that refractory coatings became not only interesting, but mandatory. The long service lives (30 minutes and up), and repeated use requirements on top of the high surface temperatures of 2500° - 4500°F, necessitated designing structure surfaces which are stable in air at these temperatures. Thus, for perhaps the first time, the feasibility of a vehicle design was dependent upon refractory protective coatings. These coatings can be conveniently categorized into two general areas by temperature requirements, namely those useful below 3000°F and those useful above 3000°F. The systems useful up to 3000°F are the coated molybdenum and columbium alloy systems and coated graphite. Those useful above 3000°F are generally the refractory oxides in various composite designs. Since radiation as a thermal protective system is dependent upon maintaining a very high surface temperature for efficient re-radiation of thermal energy, these designs are very dependent upon internal thermal insulation for payload protection.

However, these insulation systems are very dependent upon specific design trade-offs and cannot be considered here except in general terms. It should be noted, however, that in many of these refractory composites considerable insulation is provided by the composite itself which helps pay for its weight.

To illustrate the vehicle application discussed here, figure 1 illustrates a typical re-entry glider. The various critical areas of interests are the nose cap with maximum temperatures to over 4000°F, the leading edges with maximum temperatures to 3000°F, and the various skin areas with maximum temperatures below 3000°F. These are indicated in figure 2.

With these typical structural applications in mind, the various materials systems can be discussed.

Coatings for Refractory Metals

The attractive high temperature properties of the current refractory metal alloys of molybdenum and columbium have provided the designer with an additional 1000°F above the 2000°F limitation of the super alloys in the design of structural components. This allowed designers to use familiar sheet metal construction concepts in building re-entry vehicle components, rather than forcing them into the distasteful task of learning to design with the brittle, unpredictable ceramics available. It is well known that all the refractory metal alloys require coatings for protection from oxidation. This has greatly increased the difficulty in design and construction.

Nevertheless, the very encouraging results from coating development programs have provided several families of coatings with sufficient protection for current requirements. This now allows the use of Mo and Cb alloys for high temperature structural components.

These coatings can be described as "diffusion coatings". Several elements, such as Si, Cr, Al, Ti, etc, are deposited on the surface of the metal, and concurrently or subsequently heat treated to allow diffusion and to produce the intermetallic systems which are the coating. The two generally used deposition methods are cementation and slurry or dip coating. The cementation method, taking its name from its similarity to carbonizing, has been the most actively pursued technique especially for moly alloy. Several variations of this technique exist but the basic principles involved are essentially the same. In pack cementation, the part to be coated is packed in a retort with a powder consisting of the coating elements such as Si and Cr, an activator or carrier such as I_2 or a halide compound and an inert filler such as Al_2O_3 . The retort is then closed, sealed, purged, and heated to 1900°F for several hours. During the heating period the halide vapors carry the coating elements to the metal surface and deposit them. At the high temperature of processing these elements then diffuse into the surface and form the intermetallic compounds which constitute the coating.

In the slurry and dip processes, the coating elements are deposited by coating the part with a slurry, or by dipping the part into a molten bath of the mixture. The part is then heat treated to allow diffusion to occur.

These coatings have not been a panacea for the problems of using refractory metals, due to characteristics such as their low temperature brittleness and the complication they add to the manufacturing operations. Nevertheless, the availability of these coatings has allowed the development, manufacture, and successful testing of many types of high temperature structures for glide re-entry vehicles. The following illustrations show the current high temperature structural applications of coated refractory metals.

Figure 3 typifies the "hot structure" concept where the refractory metal acts as a non load carrying high temperature skin operating at over 2500°F and the true structure a superalloy is kept to some reasonable temperature below 1800°F by insulation.

Figure 4 typifies the cooled structure concept with a coated refractory metal skin operating at over 2500°F attached to a well insulated, cooled Al structure operating at 200°F.

Figure 5 illustrates a complex, coated structure which **skin panels** could operate at 2500°F.

The current capabilities of coatings for moly and Cb alloys provide very reasonable lives in air of many hours at 2700° - 2800°F for molybdenum and 2500° - 2600°F for Cb, with useful lives at 100° - 200°F high temperature.

Figure 6 typifies in generalities the reported lives of various systems. It also indicates that specific systems do indeed have very sharp maximum temperature capabilities, where protection ceases. Also, and more important, there are no systems available with useful lives much over 3000°F.

Graphite

The primary problem pertaining to the use of graphite in air at high temperatures is the same as that of the refractory metals namely oxidation. The coatings available for graphite are somewhat similar to those of the refractory metals. They are silicide coatings applied by a diffusion process.

Current uses for graphite in these applications are limited to temperatures below 3000°F because of the coating systems available. Because of this limitation, the attractive properties of the commercial graphites cannot be fully exploited. Moreover, the difficulties, involved with designing with a sensitive, brittle material often cannot be substantiated if use temperatures cannot be over 3000°F. Therefore, in the past graphite has been used mostly in composite structure where it acts as a transition material - useful at only slightly higher temperature than coated refractory metals but much easier to work with and perhaps lighter than the refractory oxide systems.

The recent activity in the pyrolytic deposition of graphite and graphite alloys have produced the only truly new class of engineering materials. The potential of these materials has been demonstrated in many short time applications. However, chemical compatibility and long time stability at high temperatures remains to be determined. More important, however, is the fact that design concepts have yet to be developed to provide mechanically reliable structural components of these brittle materials.

Sprayed Coatings

Certain applications in vehicles, such as the nose area and leading edges may require additional coatings to overcome the 3000°F limitation of current coatings for refractory metals and graphite. Here the objective is to provide a thermal insulating refractory oxide top coating capable of withstanding the higher temperatures. These could generally be flame or arc sprayed over an oxidation protective coating. The main problem is the usual poor match of thermal expansion between the coating and the substrate, resulting in susceptibility to thermal shock and consequent spalling of the top coat. Several techniques such as the graded coating and the multi-layer coating have been developed to overcome this problem. These techniques modify the thermal expansion characteristics of the coating by varying its composition so that at any point it is able to withstand the reduced resultant thermal stress.

Figure 7 illustrates the concept of graded coatings where the composition of the coating is varied from the substrate to the surface to remove the critical interface problems.

Reinforced Ceramics

The use of solid ceramics in structural components of advanced vehicles has been limited again by a lack of understanding of design techniques for brittle materials. Although the oxide ceramics offer the only materials stable at high temperatures in air, their extreme shock sensitivity and tendency to crack catastrophically have precluded their use as monolithic structural components. Many efforts to use oxide systems as insulating, radiating structural protective systems have resulted in the development of several types of metal reinforced ceramic systems. Super alloys, coated, and uncoated refractory metals, and noble metals have been used in a great many configurations as the reinforcement for various oxide systems. These concepts are typified in the following illustrations: figures 8, 9, and 10.

The bulk of reinforced ceramics concepts are dependent upon chemical bonding techniques for the oxide systems. This is true because of the high sintering or hot pressing temperatures generally required for refractory oxides. A chemical bonding is necessary for two reasons: first, the temperatures involved in sintering Al_2O_3 and ZrO_2 systems would melt all but the refractory metals and preclude the use of superalloys. Second, with a metal backing the thermal stresses set up upon cooling from the sintering temperature would fail the composite. Also, chemical bonding allows the fabrication of complex and large components since many application techniques such as spraying, trowling, casting etc., may be used. Chemical bonding generally involves mixing the powdered oxide with an acid such as phosphoric acid, forming the desired shape, and curing the system at a temperature anywhere from room temperature to 1000°F . This develops a hard, strong body which retains its strength and does not shrink when heated to high temperatures, if done properly.

The oxide systems used are generally based upon Al_2O_3 systems for use up to 3500°F , and ZrO_2 systems for use up to 4500°F . In many systems these oxides are alloyed with other metal oxides such as Cr_2O_3 and/or rare earth oxides to increase the emittance of the system. Oxides such as ThO_2 and HfO_2 are used for very high temperature systems. Also, many oxides are used in these ceramics alloys to control and adjust the thermal expansion characteristics.

These systems are being proposed for many applications and are being evaluated for vehicle applications such as skin panels, leading edges, and nose caps. The following illustrations show some of these concepts: figures 11, 12, and 13.

The Role of Emissivity

These systems offer promise for long time use primarily because of their stability at high temperatures in air. The oxide systems of greatest interest are good insulators — to keep internal temperatures as low as possible. Since these are vehicle applications, minimum weight is always the major objective, therefore, the system must provide the maximum thermal protection for a given weight. With a given designed set of conditions, the actual surface temperature is a strong function of its emittance as illustrated in figure 14. There are then, two requirements for high emittance. First these systems are used close to their maximum temperature or melting points; a lower E than desired could cause the material to melt at the maximum expected condition. Second, with a given environment and composite, a lower E than expected, with the higher surface temperature, would allow more heat to be transmitted through the protective system thus upsetting the internal heat balance and overheating the payload.

Figure 15 shows a typical time-temperature trajectory. It can be seen from this, how the usefulness of a system is dependent upon a high, stable, known emittance.

Future Prospects

1. Coatings for refractory metals and graphite must be developed with useful lives to at least 4000°F . If W and/or Ta alloys are to be used in structures they must be used at very high temperatures to offset their very high density. Also, as the characteristics of current coatings become better understood, compositions will be developed or modified to provide high emittance long lives, and high reliability.
2. Oxide ceramic systems will be developed for use at higher temperatures through the use of ThO_2 , HfO_2 , etc. systems. Emittance control techniques will be developed which

will provide a high stable emittance through alloying with systems such as the rare earth oxides. Finally chemically bonding techniques will provide a wide range of ceramic systems for use with new reinforcement materials and techniques. The object here will be low conductivity, long lives, and controllable properties.

3. Current developments in the pyrolytic deposition of materials are providing an entire family of radically new and different materials. In addition to the popular pyro-graphite with its extremely anisotropic properties, there are alloys of pyro-graphite with elements such as Boron which offer a wide range of properties. Also other compounds such as BN being produced this way appear to offer radically different characteristics than the more common forms. Many of these materials may offer sufficient oxidation resistance for consideration in these applications. However, these are still brittle materials subject to catastrophic mechanical failure, so that considerable development must be done in design concepts and material characterization before confidence will be placed on their use.

4. Oxidation resistant materials are being developed which will be useful structural and protective materials without the use of coatings. These will allow simpler, more reliable designs to be used because of their self protection. A few very promising systems are currently being developed, and several are available. Ceramic bodies are being developed which like SiC and MoSi₂ are self protective and may be useful over 3500°F in air. There are interesting developments in cermet-like materials that may behave like metals and yet be oxidation resistant to 3000°F.

5. Emittance control will be provided by a better understanding of surfaces and surface effects, by composition variabilities built into the composite systems, and perhaps as important, through the use of more realistic, more accurate emittance measuring equipment.

BIBLIOGRAPHY

1. "Development and Evaluation of Insulating Type Ceramic Coatings", WADC Technical Report No. 59-102, E. W. Blocker, C.A. Hauch, S. Sklarew, and A. V. Levy (November 1959)
2. "Development of a Cementation Coating Process for High Temperature Protection of Molybdenum", ASD Technical Report No. 61-241, P.J. Chao, B. S. Payne and D. K. Priest (June 1961)
3. "Summary of Second High-Temperature Inorganic Refractory Coatings Working Group Meeting", WADC Technical Report No. 59-415, D. Roller (June 1959)
4. "Private Communication", J. R. Myers, Dyna-Soar Engineering Office, ASD (June 1961)
5. "Development of Reinforced Ceramic Materials Systems", W. Sterry, L. Stejskal, and J. Gunderson, Boeing Airplane Co., WADD Technical Rpt. No. 60-491 (May 1960)
6. "Structural Materials Research for Manned Lift Re-Entry Vehicles at Materials Central, WADD", D. H. Cartolano, A. Olevitch, J. R. Myers, presented at American Institute of Chemical Engineers Conference, Washington, D. C. (Dec. 1960)
7. "Leading Edge Segment Development Program", G. C. Irons, Marquardt Summary Report on Project No. 502 (March 1959)

8. "Refractory Metals Structural Development Program", Quarterly Progress Reports on Contract AF 33(616)-6578, McDonnell Aircraft Corp., (Sep 59-Oct 60)
9. "High Temperature Coatings for Aero-Space Applications", WADC Technical Memorandum No. WCLT TM 59-104, J. R. Myers (Nov. 1959)
10. "High Temperature Composite Structure", Quarterly Progress Reports on Contract No. AF 33(616)-7497, The Martin Company (Oct. 1960 - Apr 1961)

TYPICAL GLIDER

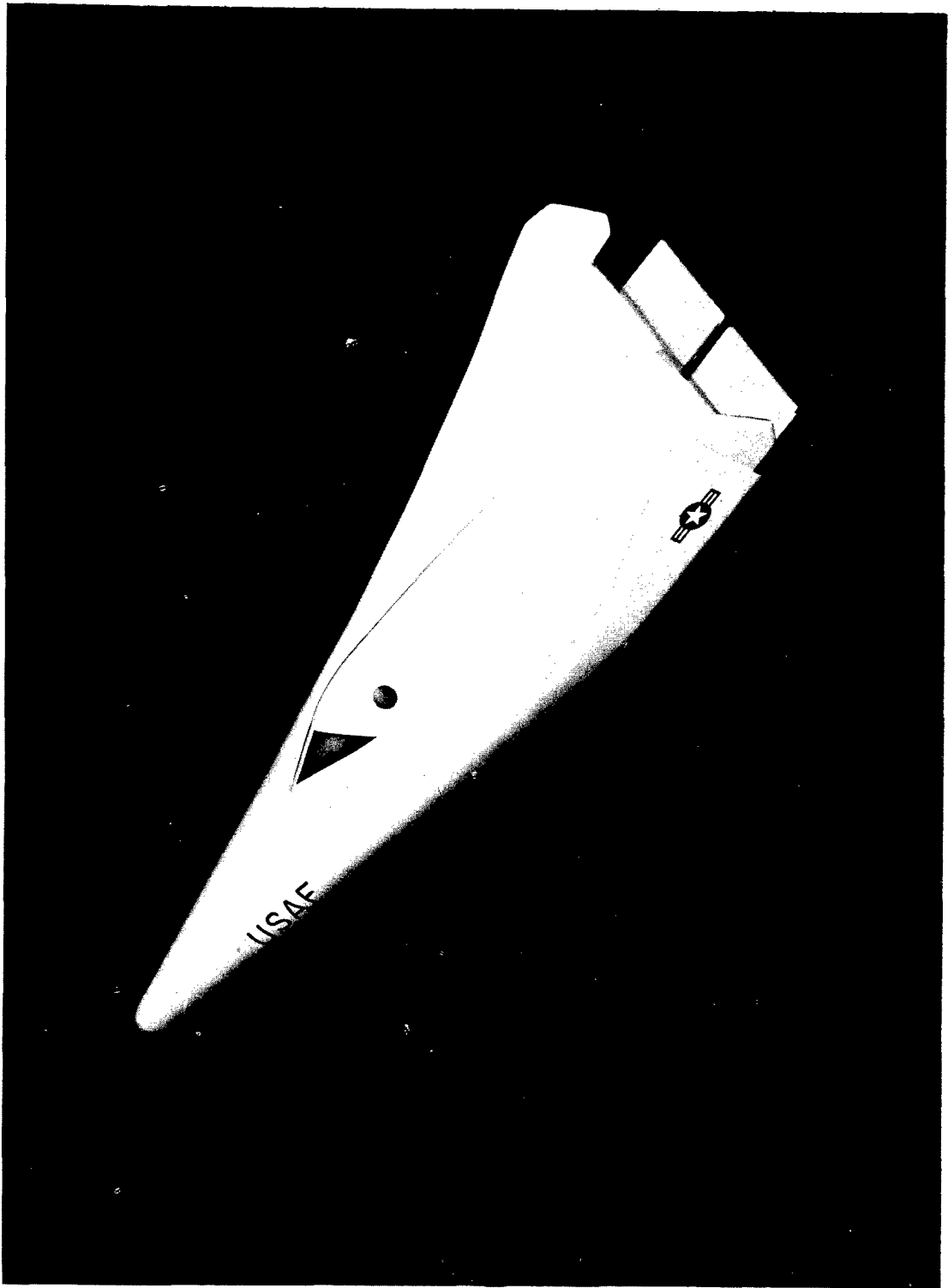


Figure 1.

**ESTIMATED SURFACE TEMPERATURES OF A GLIDER
DURING REENTRY FROM 26,000 fps.**

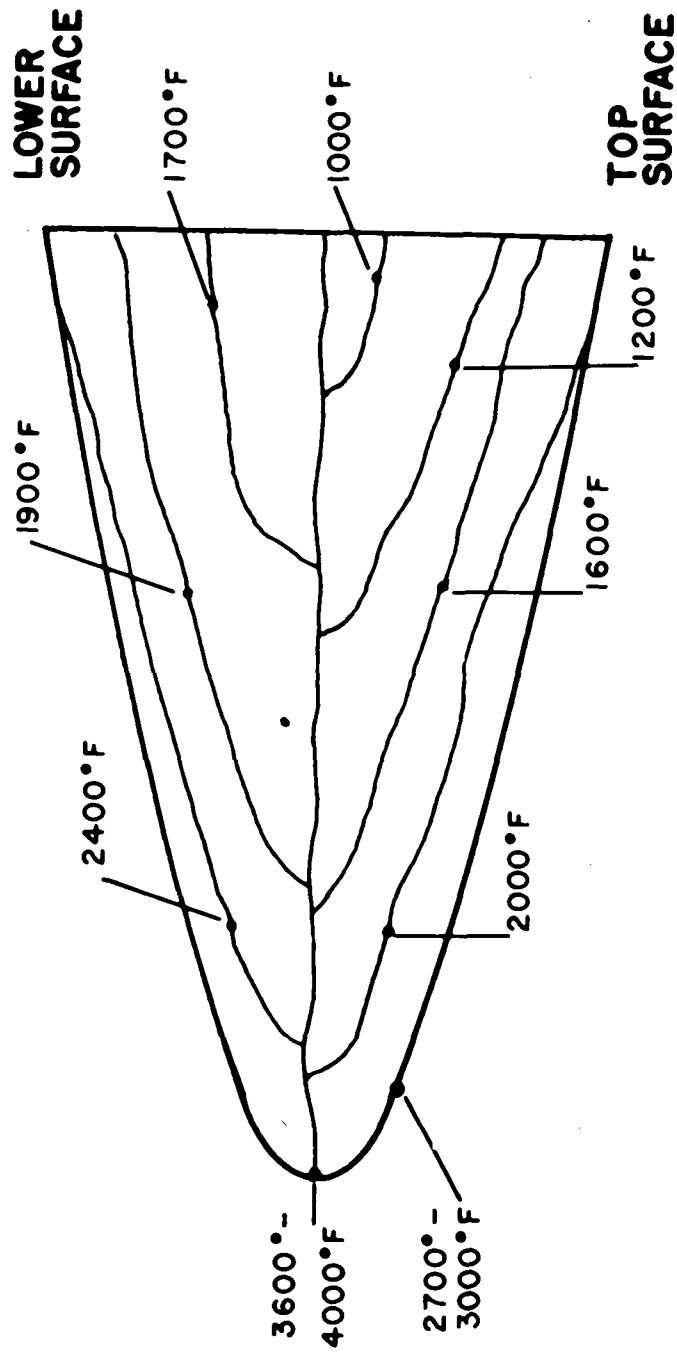


Figure 2.

HOT STRUCTURE

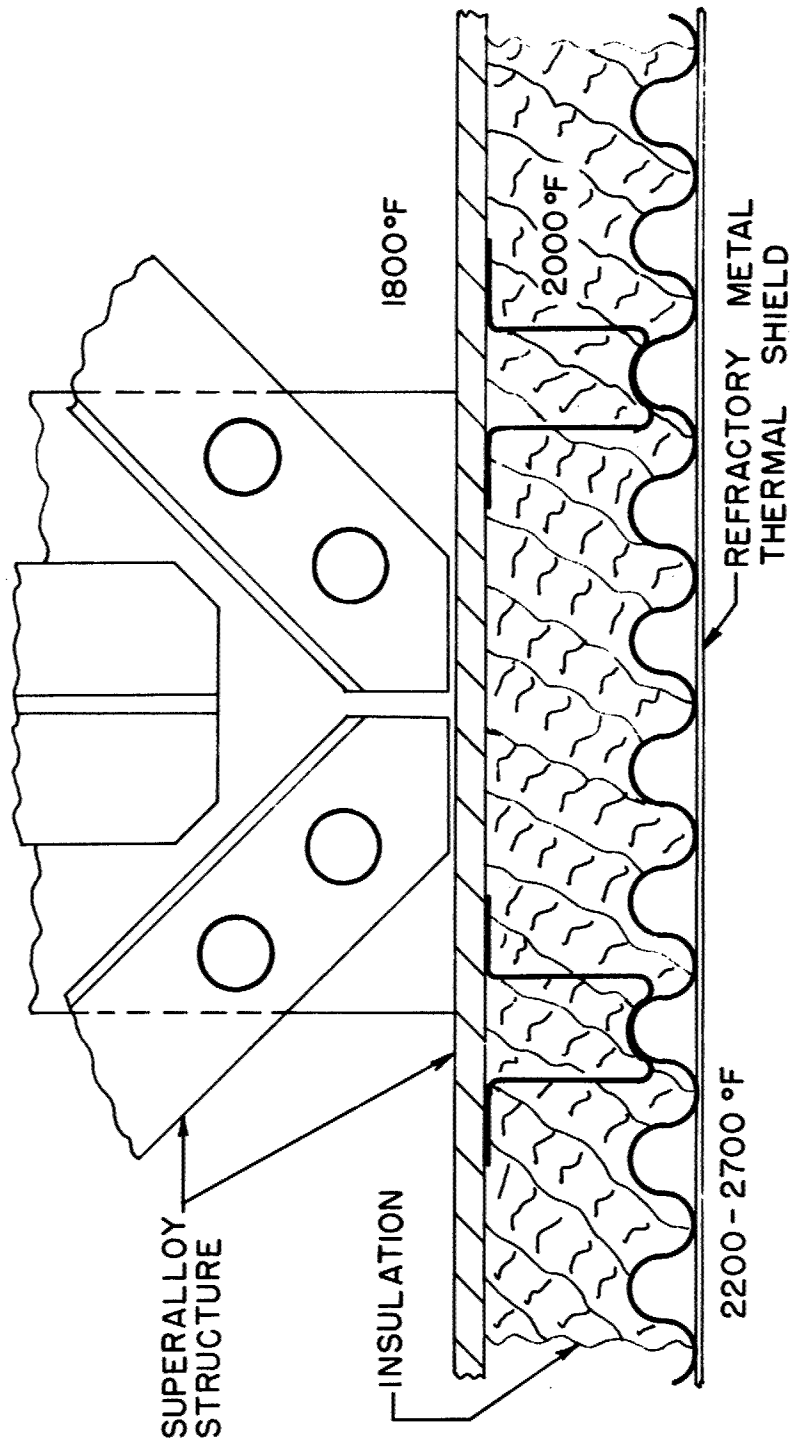


Figure 3.

INSULATED & COOLED STRUCTURE

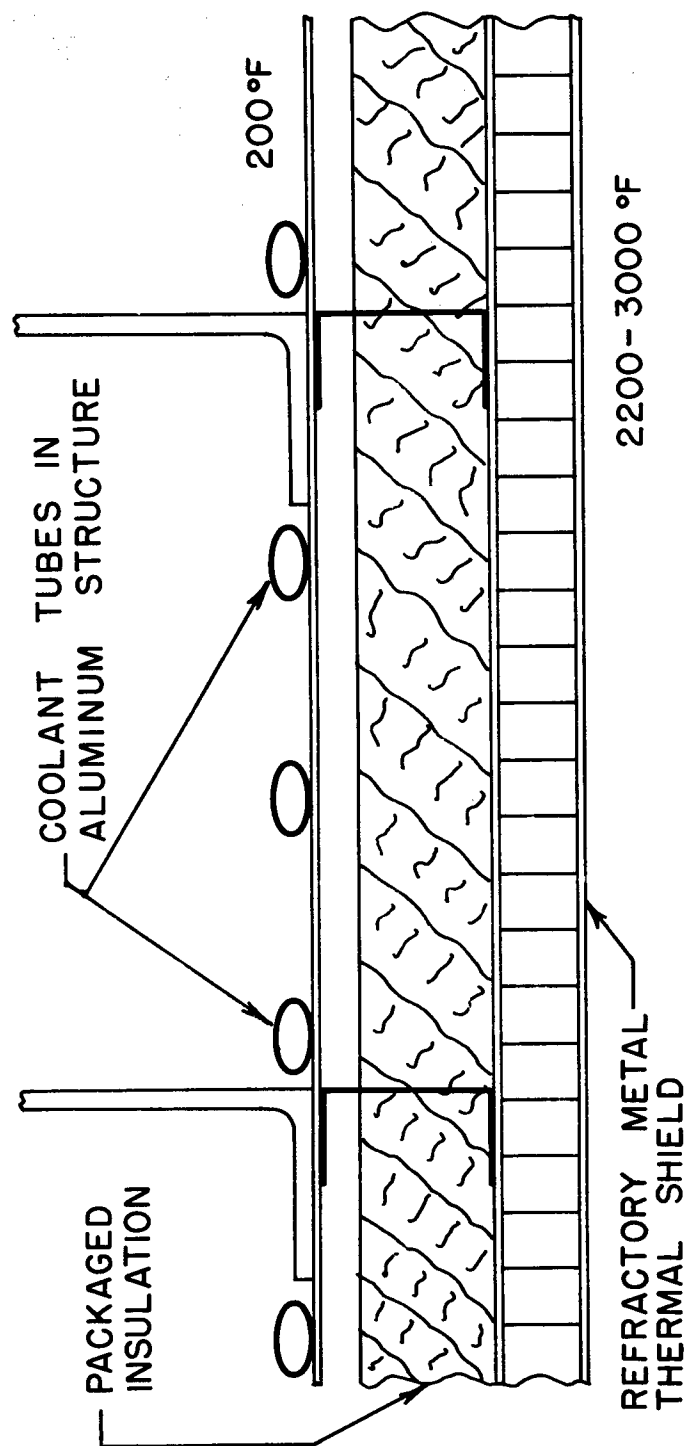


Figure 4.

STRUCTURAL COMPONENT

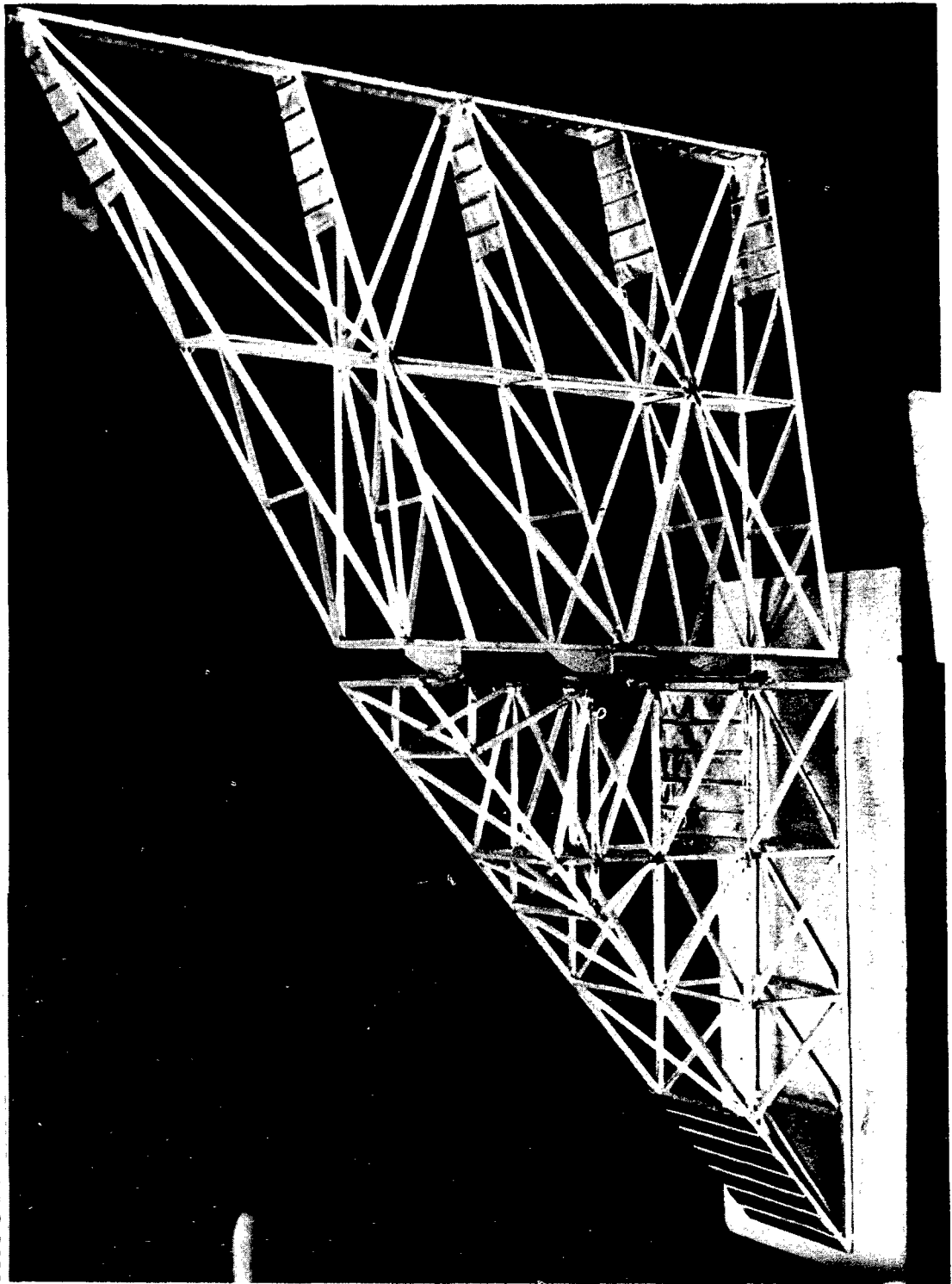


Figure 5.

USEFUL LIVES OF COATINGS IN AIR

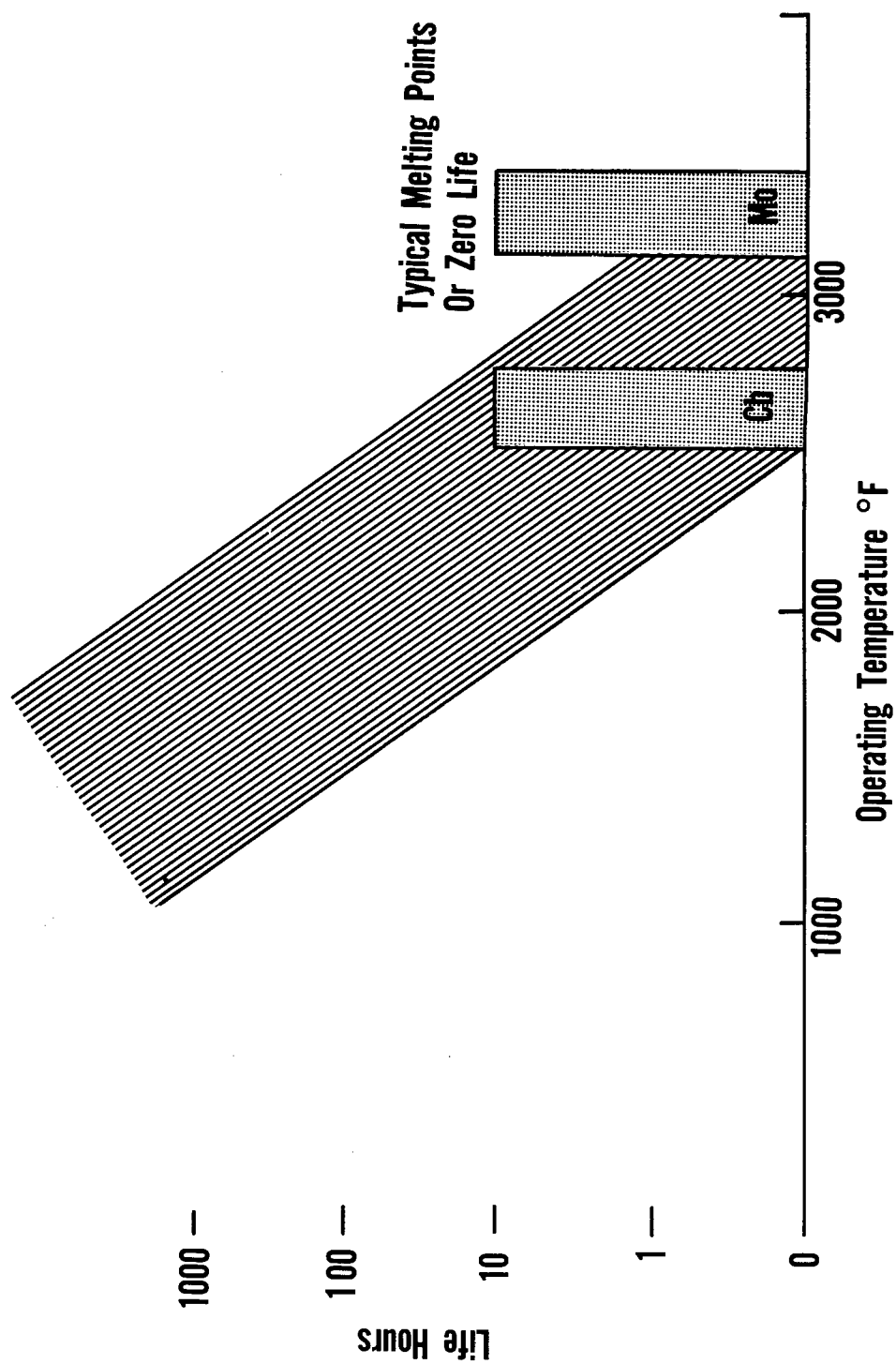


Figure 6.

GRADATED COATINGS

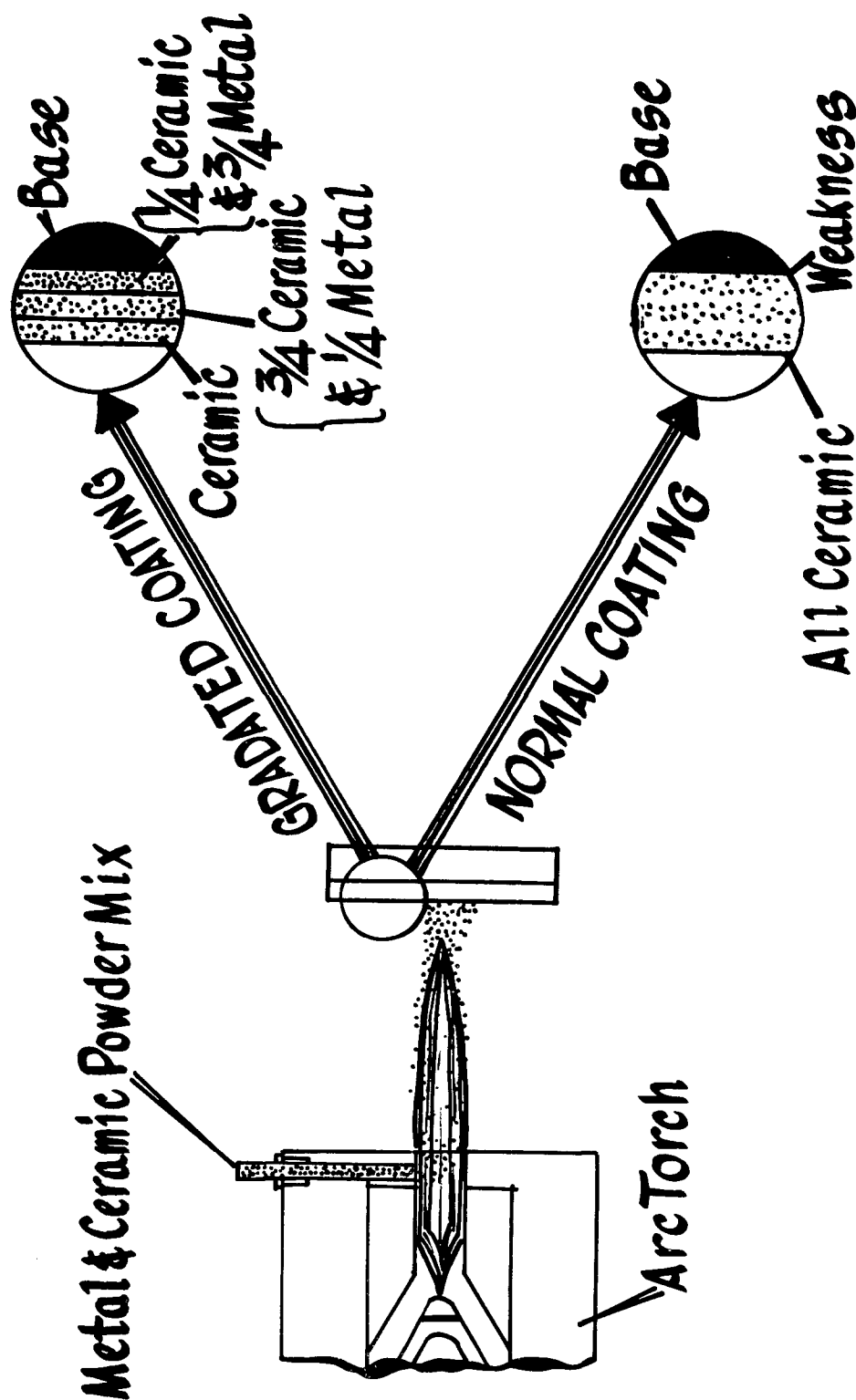


Figure 7.

CERAMIC FILLED HONEYCOMB

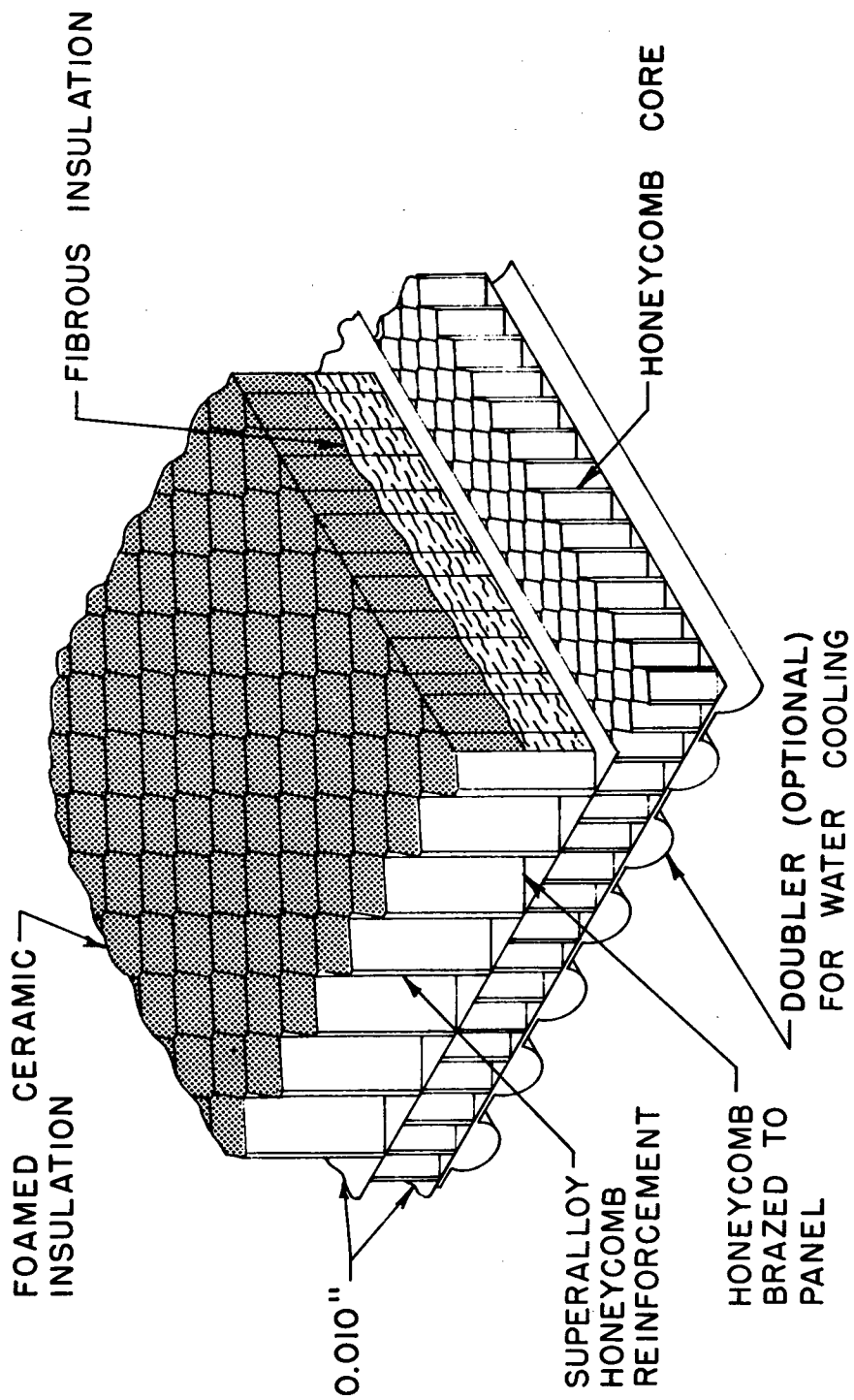


Figure 8.

TROWELED IN PLACE CERAMIC COATING



SYNTHETIC ANCHOR
PATTERN

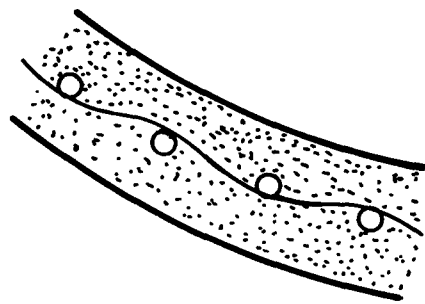


ALUMINUM PHOSPHATE
BONDED ALUMINA

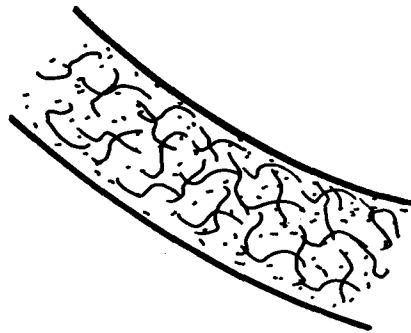
SCALE 1"=1" 0 1 2

Figure 9.

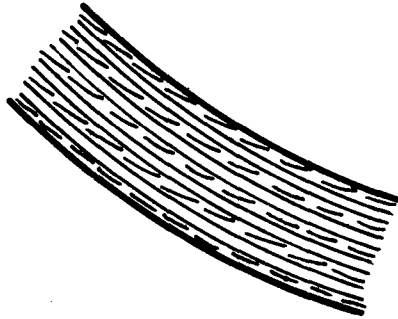
METAL- CERAMIC COMPOSITES



METAL SCREEN
REINFORCED
CERAMIC



METAL FIBER
REINFORCED
CERAMIC



CERAMIC - METAL
MULTILAYER

Figure 10.

SKIN PANEL

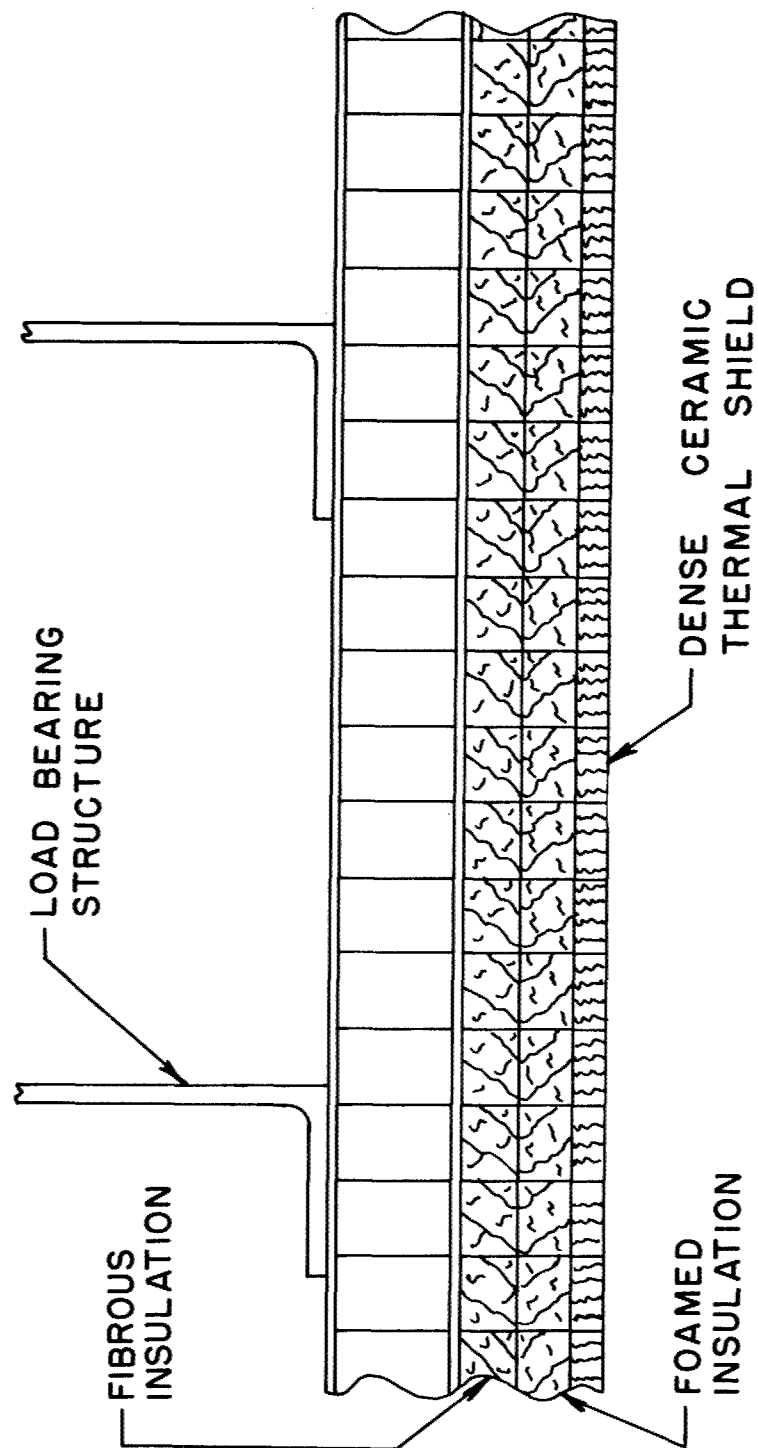


Figure 11.

METAL REINFORCEMENT FOR LEADING EDGE

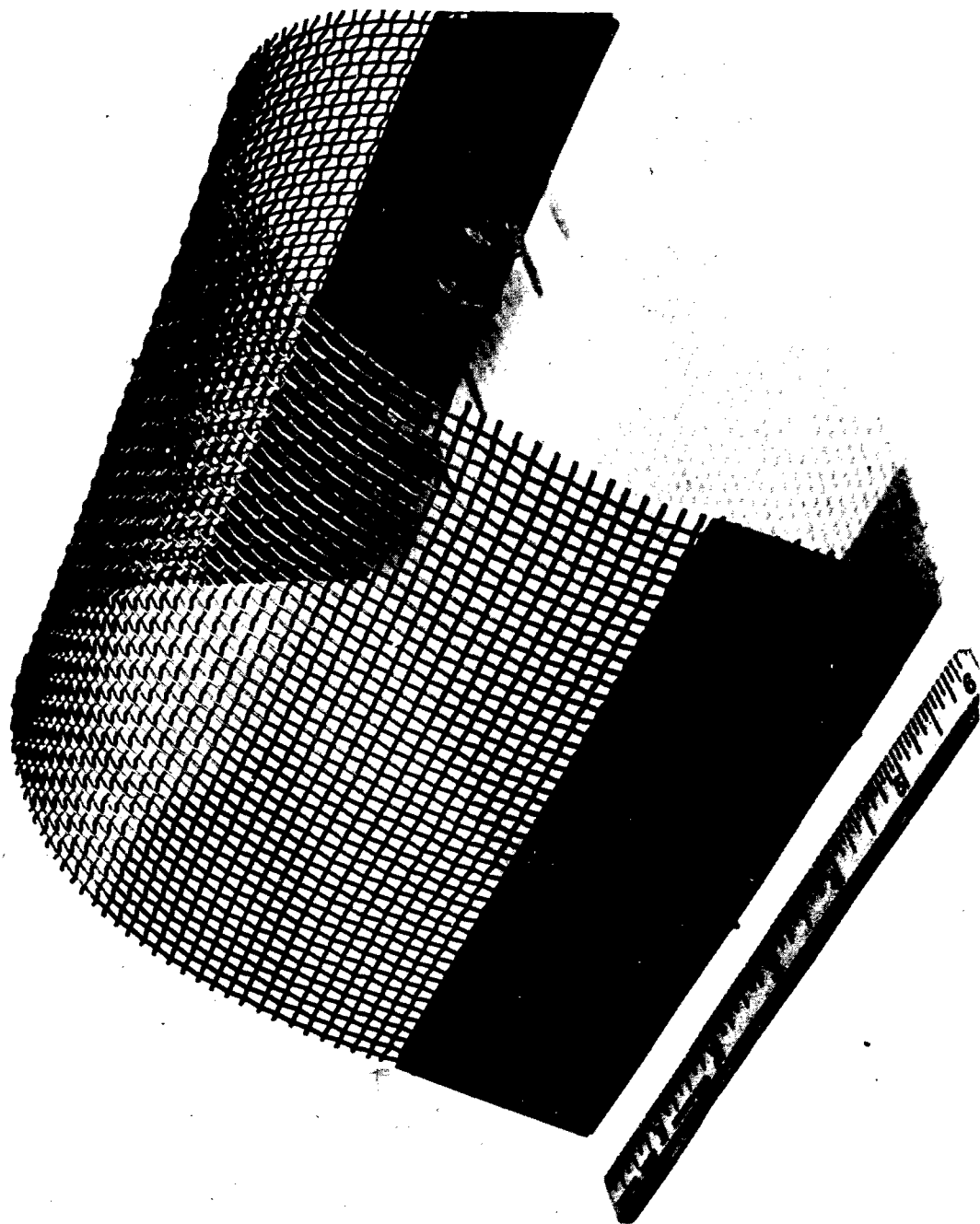


Figure 12.

REINFORCED CERAMIC LEADING EDGE

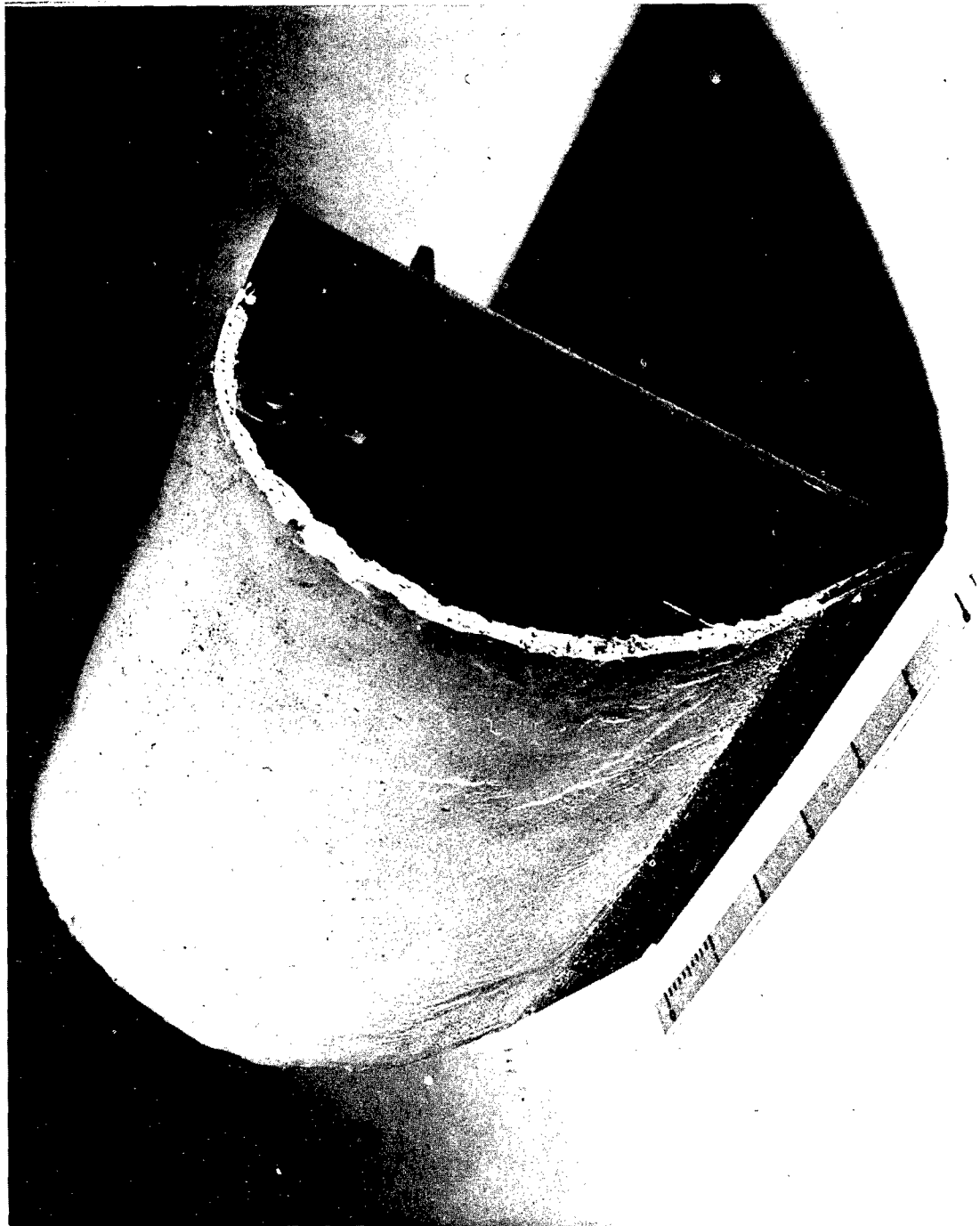


Figure 13.

INFLUENCE OF EMITTANCE ON SURFACE TEMPERATURE

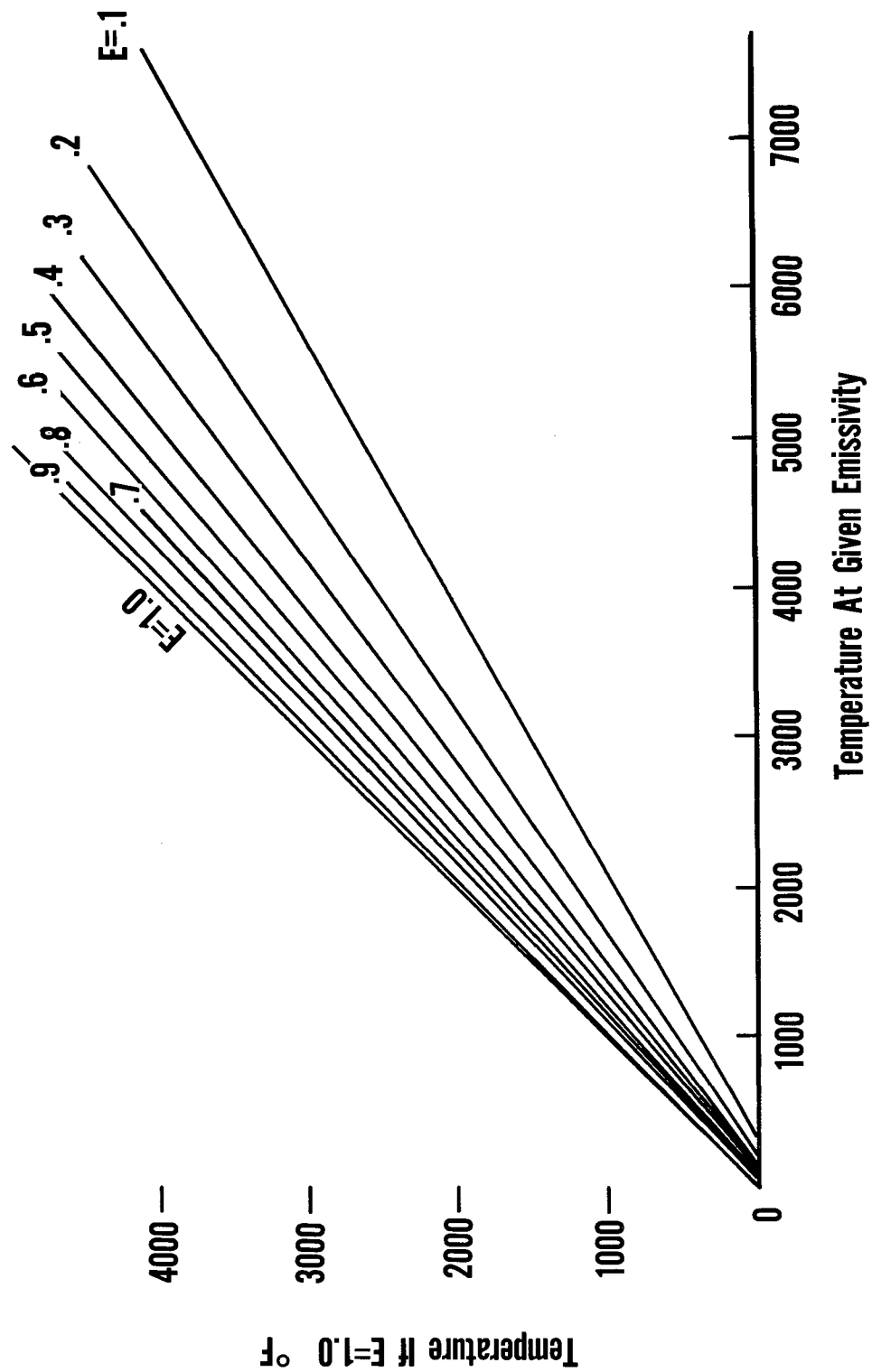


Figure 14.

THE EFFECT OF EMITTANCE ON VEHICLE PERFORMANCE

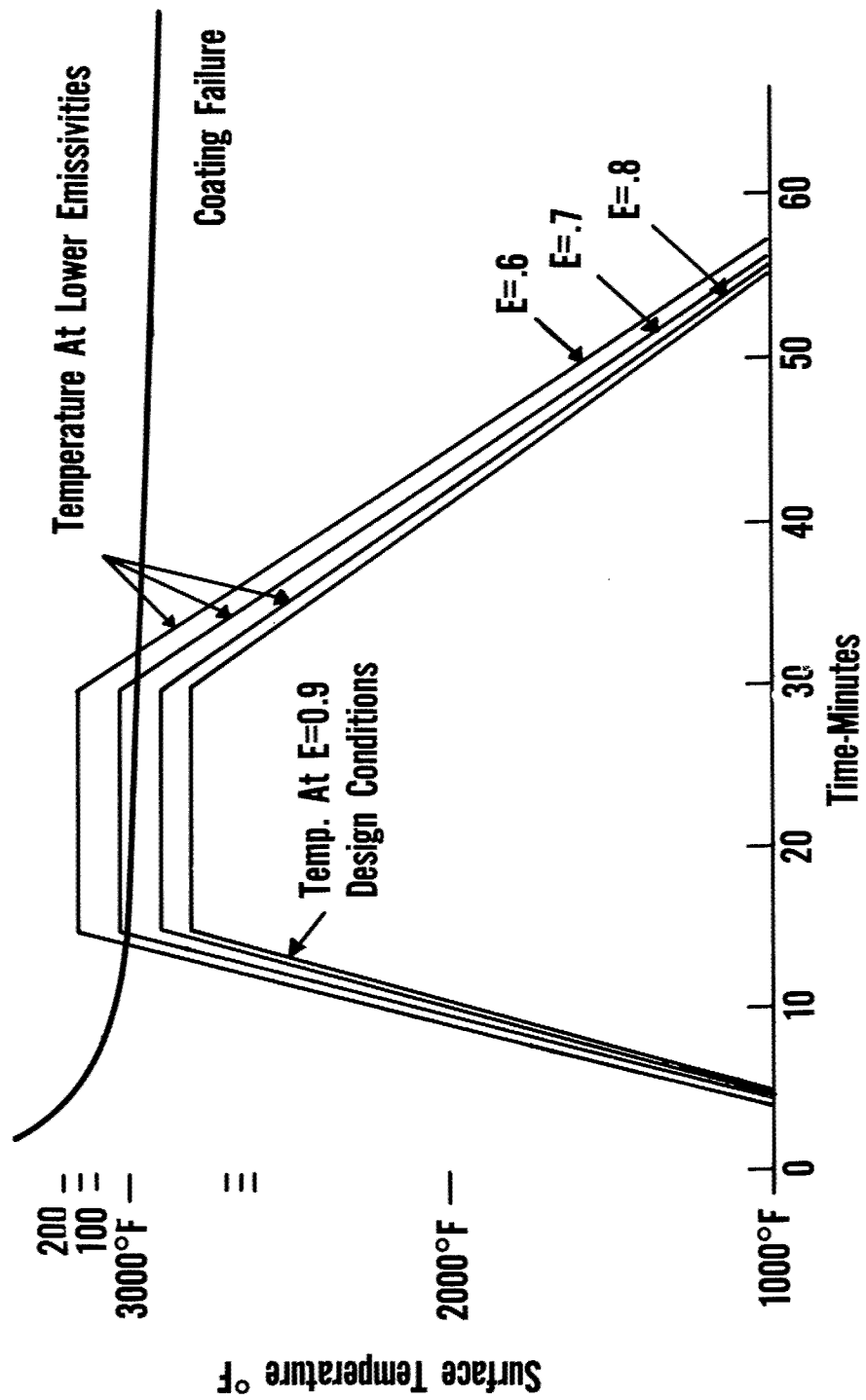


Figure 15.

RADIATION EFFECTS

Chairman

Capt R. J. Vossler

Speaker

Dr. B. Manning (AFCRL)

Dr. J. Radell

Mr. R. Hickmott

Panel Member

Mr. W. Griffin

THE EFFECT OF RADIATION ON SOLID STATE MATERIALS AND DEVICES

Dr. Bernard Manning

Air Force Cambridge Research Center

Introduction

The effect of radiation on solid state materials and devices is indeed a broad subject area to review, not that there is a lack of data but rather the opposite, there is a plethora. Specific data on specific devices taken under specific conditions has been tabulated, compiled (1), and filed, and is certainly available to all (2). However, there is more than a suspicion that the data, except for frozen electronic systems, is little used. There are many reasons for this: the obsolescence of the device itself by the time the test data is made available; the variation in the device characteristics caused by the vagaries of manufacture, or deliberate change of method or of contact materials or of potting compound; the use of the device in new combinations; the uncertainty of whether the conditions of test actually can be extrapolated to the presumed conditions of use of the device under consideration; and probably of least importance, ignorance of the existence of the test data in the first place.

The Air Force has, for some time, had to have knowledge of how off the shelf items and systems would function under various prescribed conditions. This has not been what might be called a research program but rather an engineering test program to determine the limits of utility of the various electronic systems upon which our defenses depend. Originally, this test approach was aimed at determining the effect of atomic weapons on existing and postulated weapon systems. Gradually—with the advent of nuclear power packages and then the discovery of the Van Allen Belts, the concern with whether the moon is radioactive to an appreciable degree, and even the possibility of the existence of other radiation belts around Jupiter—requirements of the Air Force have extended to a need for basic knowledge of the effects of radiation of all types on materials and devices from which they are made. This requirement should not be construed as an immediate need to set up test facilities to duplicate radiation environments either known or imagined but rather a need to develop in detail a fundamental knowledge of how radiation moves atoms about, the range of movement of secondaries, the energy levels produced, the energy-effect and dosage-effect relationships, the permanence or additivity of the changes, and the interaction between these changes in a given material and the other environmental factors involved. In short, there is a considerable need for basic research to establish more quantitatively the fundamental theory upon which extrapolation to practical situations can be based.

In the past, the testing program has been based principally on reactor data results. Because of the complex spectrum of neutron energies and gamma ray energies present in such reactors the data has been difficult to interpret in terms of fundamental events. An additional complication has been that the neutron energy spectra differ in the different reactors and in different locations in the same reactor, and variation in temperature too has led to additional complications. The tendency has seemed to be to lump the results under a series of generalizations which may be paraphrased thus: solid state devices are sensitive to radiation, and transistors are very sensitive to radiation. As with all generalizations, this is an oversimplification and indeed a harmful oversimplification since it stultifies further investigation. The reactor data is crude, but no more

crude than the conditions under which the data was obtained. Unfortunately, in this paper there is no time for other than generalities but these may indicate some of the possibilities. The effects of radiation on certain classes of materials and devices may be examined through a brief review of how incident radiation interacts with materials. There are two types of occurrences, ionization and atomic displacement; the latter is accompanied by the former but ionization need not be accompanied by displacement. Gamma rays and electrons (beta rays) will produce ionization, but atomic displacement usually will not occur if the energy of the ray is less than some minimal amount. This minimal energy for atomic displacement, the threshold, is dependent upon the material in which the event takes place. The threshold is not truly a singly valued step function but rather a statistical function of lower energy. Gamma rays function in much the same way as electrons because the energy of the ray may be given up in Compton scatter to an electron on collision and then this energetic electron is, except for its origin, identical to a beta ray. The efficiency of conversion, by collision, of the gamma ray is quite low and is dependent on the electron density of the target material. For our purposes gamma nucleus interactions may be neglected.

Radiation Interactions

Our consideration will now be given to the behavior of neutrons, protons, and other particles during radiation. Uncharged neutrons will approach any target, but will not produce an effect on other particles except subsequent to a collision. Neutrons will usually collide with a nucleus rather than with an electron because of their relative sizes. After collision, the now charged energetic particle goes speeding off, collides with other nuclei, dislodging them as well as many electrons. In the same manner, protons impinging on a target will also collide with nuclei and dislodge electrons. Charged particles are more effective in freeing electrons from their bonds when they are moving slowly because of the longer time available for a reaction to take place. Neutrons will frequently displace 10^3 to 10^4 or more atoms; protons will displace somewhat fewer atoms than neutrons; electrons will displace 1 to 10 atoms; and gamma rays will displace one or a few atoms if there is conversion.

The most noticeable effects of these interactions during radiation are the resultant crystalline defects and the energy released from the increased number of electrons free to move about until trapped. The first named, atomic displacement, produces the permanent effects while the latter generates only temporary effects. Nuclear transmutations and its delayed effects are considered, for our present discussion, to be only minor.

Ionization events, resulting from the released energy, have a relaxation period during which the electrons in the conduction band revert to a more stable energy level. The number of electrons placed in the conduction band is a function of the kind of radiation causing the ionization and the number of incident quanta or particles (dose).

Radiation Effects

The defect density is a function of the kind of particle while the number of defects reflects the amount of dosage.

The transient effects produced in electronic devices may cause other effects at a considerable distance from the particular radiation sensitive device since all parts of an electronic circuit are interrelated. The immediate effect of transient radiation pulses is revealed by the presence of conduction electrons which may provide leakage paths

and/or alternate conduction loops. The result may be a noise signal induced in the circuit where a pulse would not normally be or an alteration of signal normally present. The duration of the transient effect itself normally does not last much longer than the radiation pulse and the extent of the alteration is somehow related to the pulse intensity (dose rate).

Permanent effects, residual after the occurrence of the pulse, are dependent on the type of material in which the radiation-induced event occurs and result in such phenomena as increased resistivity (e.g., when n-type germanium is converted to p-type), increased brittleness in conductors, variation in the frequency of oscillation of quartz crystals, induced voltages, and chemical changes. Permanent effects are cumulative and present data indicates that they are largely independent of dose rate.

The devastating effects of radiation are so great that it is not possible to develop materials which will not be affected by radiation. This point is well illustrated by consideration of the fact that electronic binding energies are measured in no more than tens of electron volts and that the energy required to move an atom by collision with an electron, in hundreds of kilovolts, but the energies of ray particles are described in millions of volts.

Protection From Radiation

Protection from radiation may be accomplished in more than one way; shielding and design are two which have been studied. In general, the cheapest and lightest shield is supplied by distance from the source because radiation intensity decreases with the square of the distance between source and target (except for beamed particulate radiation). In addition to distance, mass is the radiation shield protection most frequently used, and may be attained by simply supplying an inactive mass.

Devices and circuits can be designed to accommodate the effects of radiation up to certain stated limits without excessive deterioration in functional performance. This can be done by again using the protection of distance by locating less radiation-sensitive components on the outside of the circuitry. It can also be done by incorporating redundancy or parallelism into the design or by such tricks as blocking out, during pulses, portions of the system by radiation sensors.

A combination of materials knowledge, circuit design, and shielding design can be parlayed into circuitry which will meet requirements not only of function in atom bomb radiation fields but in Van Allen Belt type radiation or in proton flares and the other radiation fields which may be encountered. Even with the relatively simple types of radiation environments which we now know exist there are considerable complications.

Radiation Environments

We will start our discussion of specific radiation environments with a discussion of perhaps the simplest and most easily shielded against, the recently described Van Allen Belt. (Its characteristics are summarized in table 1.) The protons of this belt constitute a hazard to solar cells which do not have a protective layer above their active surfaces. Electron bombardment in the Van Allen Belt reduces the short circuit current in p-n solar cells. Expected lifetime of a solar cell in a circular orbit at an altitude of 2000 miles would be about 2 months unshielded and 5 months if shielded. The protons in the Van Allen Belt are relatively easily stopped, however: a sheet of aluminum with a thickness of 0.062 cm (.167 gms/cm²) is sufficient to stop protons of 10 Mev energy, and a shield of 0.21 cm stops protons of 20 Mev energy. The principle effect of the protons is

to eject electrons by inelastic collisions. Some of these would in turn attack atoms. But, consideration of the electron range in aluminum as a function of energy reveals that 0.21 cm of aluminum would stop virtually all electrons of energy below 1.5 Mev (4). However, the damage threshold for silicon is about 145 Kev, which accounts for the present trend to consider the shielding of the solar cells by a quartz plate if appreciable time is to be spent in the Van Allen Belt.

A somewhat better known type of radiation environment yet none the less difficult to describe accurately or to reproduce in test facilities is that which may be expected from a nuclear power package. Most of the testing work to date has been performed at reactors such as the two in table 2 whose results we will discuss as a "rule of thumb." Fundamentally, the observed phenomena are not varied in kind but in degree and the difficulties of interpretation lie as much in the complexities of the materials and devices as in the physical phenomena. Since the data on specific devices is available in the requisite detail from reports on file at the Radiation Effects Information Center at Battelle, we will restrict ourselves to a brief description of this phenomena as it appears in certain types of devices.

Resistors

Carbon composition resistors are extremely variable in manufacture and it is indeed a problem to determine whether changes are due to radiation, interfacial contact changes, humidity, or to some other cause. The resistors exhibit a decrease in resistivity of some 3 to 10 percent during irradiation under fast neutron flux of the order of 10^{15} , an integrated thermal flux of 10^{18} , or a gamma dose of 10^{11} ergs/gm (C). The cause of these changes may be the decomposition and carbonization of the epoxy binder. Also, the variation of effect with resistance value is related to the relative quantity of binder.

Pulsed radiation, which is available from Triga or Godiva (see table 3), produces an instantaneous decrease in resistivity as high as 86 percent for high value resistors. This large and instantaneous decrease may be due to the setting up of surface leakage paths rather than to variation of binder or bulk materials.

Deposited carbon film resistors are even more complex in manufacture and composition. Usually, the thickness of the film is within the range of the recoil of a displaced carbon atom — the higher the value, the thinner the film. It may be that the atomic displacements actually tear out chunks to decrease effective film thickness and thus increase resistivity, or that displacements actually increase the difficulty of movement of electrons in the film. (This is only an excuse for observed data not an explanation.)

Negative resistance changes are noted in resistors which are coated with methacrylate. This is excused by postulating the existence of ionization and thus alternate leakage paths.

Metal film resistors show an increase in resistivity, as expected, because atomic displacements would increase electron scatter. (A decrease would be expected, and has been observed, if coating materials other than metal are used.)

Wire wound resistors are least sensitive to radiation since they present a continuous path for the flow of electrons. As expected, an increase in resistivity results from increased electron scatter. Pulsed radiation for some reason results in a considerable resistivity increase which may be related to the induced electromagnetic field in the wire coil and the back EMF generated. This phenomena is illustrated for several types of

resistors in figure 1. Unfortunately, very little is really known about fundamental processes in resistor materials.

Varistors

Nonlinear voltage sensitive devices such as copper or selenium oxide rectifiers are also sensitive to radiation. The character of the oxide film changes easily due to collisions with particles and the secondary products of such collisions. Dosages as low as 10^{13} n/cm² produce appreciable change. The symmetrical varistors however, such as compacted silicon carbide powders have considerably greater radiation accommodation.

Capacitors

The myriad types of capacitors preclude individual consideration but some generalizations are possible. The metal film aluminum in capacitors is essentially not damaged by radiation; dielectrics and supports are. Organic dielectrics change chemically by decomposition, carbonization or polymerization. Inorganic dielectrics are much more stable. Electrolytic capacitors containing boron, which has a high neutron-capture cross section, have low radiation tolerance. Solid dielectrics of aluminum oxide, magnesium oxide, and boron nitride undergo little change in a static radiation flux. A decrease in leakage resistance accompanies a pulse because of the ionization in the dielectric.

Transformers

Transformers are capable of withstanding neutron doses in the order of 10^{17} /cm² without marked change in characteristics, provided no mechanical change takes place. Potting compounds, usually organic, undergo chemical changes and become gassy. The organic insulation resistance between windings suffer similarly; hence short circuits could occur.

Infrared Detectors

Infrared detectors of the semiconductor type such as PbS, PbSe, In Sb, and thermistors have been studied both in pulsed and continuous radiation fields. The signal to noise ratio decreases after about 10^{13} neutrons/cm², decreasing essentially to zero at doses of 10^{16} . Bolometer thermistor types have the best radiation accommodation. Irradiation results in a decrease in dark resistance. Window materials such as CaF₂ tend to become less transparent but this transmission loss which can be annealed out is minor compared to the signal to noise ratio change of the detector itself.

Transistors

For purposes of study, the transistor is most satisfactory since it is composed of material of known structure, known chemical composition, and the results of irradiation are relatively easy to measure. It seems to be rather frequently rediscovered that narrow base transistors can best accommodate radiation changes. From a simple geometric viewpoint, a narrow base presents the least mass target. Electrically the narrow base transistor permits radiation injected minority carriers to pass through without recombination. Lifetime changes are a function of the recombination cross section of the defects. The data indicates that fast neutron generated defects in silicon have a larger recombination cross section than in germanium. Silicon transistors will tolerate some 10^{16} neutrons.

Conclusion

Air Force needs of the next decade are difficult to predict, but in view of the environments to which they will undoubtedly be subjected, electronic devices of all types will need to possess all of the attributes of the most highly developed present-day equipment, reliability, power conservation, compactness, as well as the added requirement of radiation compatibility. The radiation compatibility of these new devices shall evolve from a basic knowledge of the effects of radiation on materials and a revelation of their inherent characteristics by exposure to radiation. These, in turn, will project from planned programs of research and testing coordination of physicists, chemists, engineers, and military strategists.

REFERENCES

1. Pfaff, E.R., et al. "The Effects of Nuclear Radiation on Electronic Components," USAF Contract AF 33(616)-3091, Jan. 1956, and subsequent reports.
2. Radiation Effects Information Center, Battelle Memorial Institute Columbus, Ohio, Summary reports.
3. Van Allen, J., "Origin and Nature of the Geomagnetically-Trapped Radiation." Proceedings of the First International Space Science Symposium. Nice, Jan. 1960. Edited by Hilde Kallmann Bijl, North - Holland Publishing Co. Amsterdam. Distributed by Interscience Publishers Inc., New York.
4. Donnelly, M.M., "Van Allen Radiation Damage in Solar Cells," Nuclear Electronic Effects Program, Fifth Triannual Technical Note, Bell Telephone Laboratories Inc., Contract AF 33(616)-6235, Project No. 1448-50956. 15 Nov. 1960.
5. Kircher, J.F., "Survey of Irradiation Facilities," REIC Report No. 11, Battelle Memorial Institute, 30 April 1960.
6. Hammon, D.T., Chapin, W.E., Hansen, J.F., and Wyler, E.N., "The Effect of Nuclear Radiation on Electronic Components," Radiation Effects Information Center, Report No. 12, 30 April 1960.

TABLE I
VAN ALLEN BELT RADIATION³

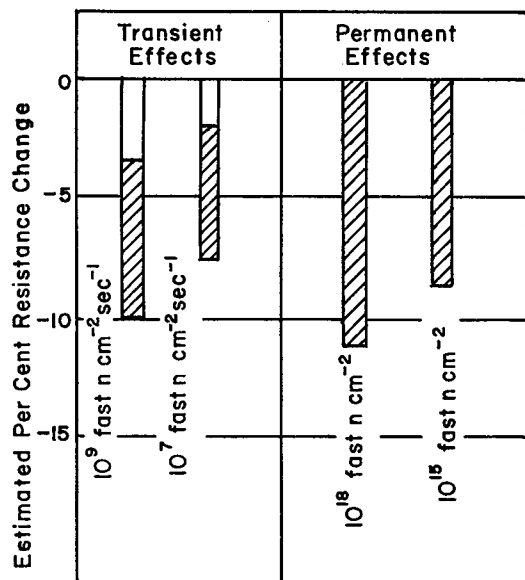
ALTITUDE	1400 - 3400 KM	8000 - 12000 KM
GEOMAGNETIC LATITUDE	$\pm 15^\circ$	$\pm 60^\circ$
PROTON FLUX	$2 \times 10^4 \text{ p/cm}^2\text{-sec} > 40 \text{ mev}$	
ELECTRON FLUX	$\sim 10^{10} \text{ e/cm}^2\text{-sec} > 20 \text{ kev}$ $\sim 10^7 \text{ e/cm}^2\text{-sec} > 600 \text{ kev}$	$\sim 10^{11} \text{ e/cm}^2\text{-sec} > 40 \text{ kev}$ $< 10^8 \text{ e/cm}^2\text{-sec} > 200 \text{ kev}$ $< 10^6 \text{ e/cm}^2\text{-sec} > 2.5 \text{ mev}$

TABLE 2
TEST REACTORS⁵

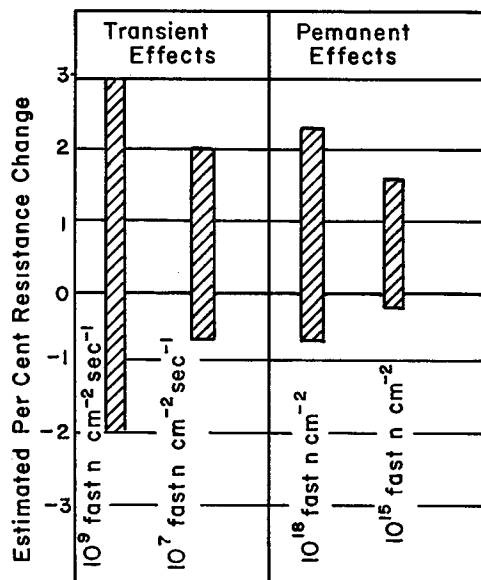
	G. E. TEST	PENN. STATE UNIV.
FAST NEUTRON FLUX (MAX)	$1 \times 10^{15} \text{ n/cm}^2\text{-sec}$	$10^{12} \text{ n/cm}^2\text{-sec}$
THERMAL NEUTRON FLUX (MAX)	$2 \times 10^{14} \text{ nv}$	10^{12} nv
GAMMA INTENSITY (MAX IN FACILITIES)	$3.6 \times 10^{11} \text{ ergs/g-hr (c)}$	$6.5 \times 10^8 \text{ ergs/g-hr (c)}$
MODERATOR	WATER AND BERYLLIUM	WATER
COOLANT	WATER	WATER
POWER AND TYPE	30 MW TANK TYPE	100kw, POOL

TABLE 3
PULSED REACTORS⁵

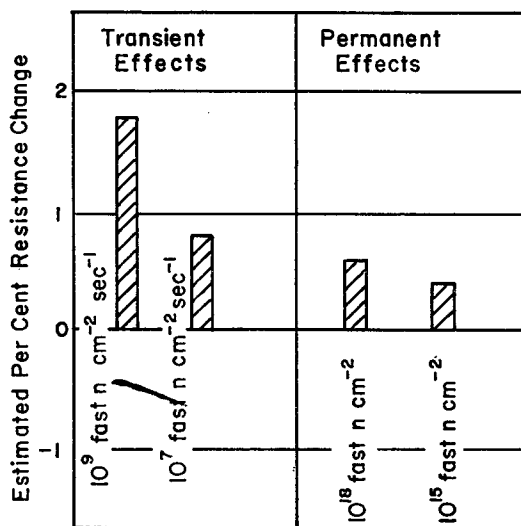
Triga (Gen. Atom)		
FAST NEUTRON FLUX (AVG.)	$4 \times 10^{11} \text{ n/cm}^2\text{-sec}$	
THERMAL NEUTRON FLUX (AVG.)	$1.6 \times 10^{12} \text{ nv}$	
GAMMA INTENSITY		
MODERATOR		
COOLANT	WATER	
POWER AND TYPE	100 kw, POOL	
PULSE	40 millisecond	15 millisecond
	FAST NEUTRON FLUX $5 \times 10^{13} \text{ nv}$	$7 \times 10^{13} \text{ nv/cm}^2$
	THERMAL NEUTRON FLUX $2 \times 10^{14} \text{ nv}$	$3 \times 10^{14} \text{ nv/cm}^2$
GODIVA II (LOS ALAMOS)		
PULSE WIDTH: APPROXIMATELY 80 MICROSECONDS AT HALF HEIGHT.		
YIELD: 10^{16} FISSIONS/BURST		
LEAKAGE SPECTRUM: SIMILAR TO U-235 FISSION MAX. AT 0.4 mev		
LEAKAGE NEUTRONS: 1.4×10^{16} /BURST.		
DOSE AT 1 METER: 30 RADS GAMMA, 370 RADS NEUTRON.		



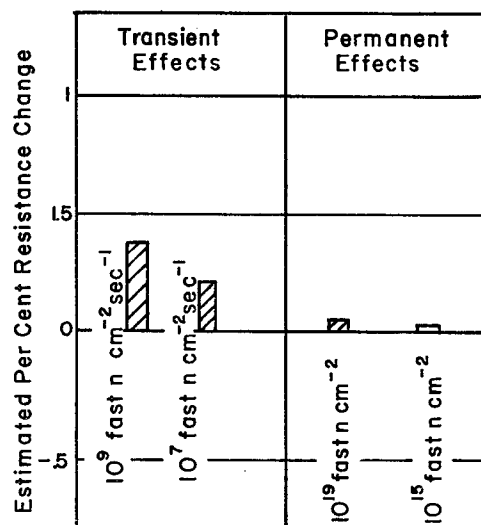
a. Carbon Composition Resistors



b. Deposited Carbon-Film Resistors



c. Deposited Metal-Film Resistors



d. Precision Wire-Wound Resistors

Figure 1. Estimated Effects of Nuclear Radiation on Carbon-Composition Deposited-Carbon- and Metal-Film, and Precision Wire-Wound Resistors

RADIATION CHEMISTRY

Roger E. Rondeau, 1/Lt USAF

Dr. Jack Radell

Directorate of Materials and Processes, ASD

Introduction

The study of radiation-induced reactions, particularly in the field of organic chemistry, has been, until recently, concerned with the transformation of reactants into products. In a typical study of a radiation chemistry system, the first step is usually a qualitative analysis of the ultimately stable products formed. This is followed by the establishment of product yields, usually in terms of G values, the number of molecules produced per 100 electron-volts of energy absorbed. This information is hardly sufficient for a complete understanding of the radiation chemistry of a system. Nevertheless, from such data have emerged various postulations of radiation mechanisms, usually on the basis of free radical paths. Such studies are not without merit. In liquid systems, a free radical mechanism postulation is completely justifiable since free radicals are frequently the most abundant radiation-induced transient species within the system. In gaseous phases, on the other hand, indications are that ion-molecule reactions appear to be a significant or even dominant mechanism of chemical change.

The physically-minded radiation chemist has become more intensely concerned with reaction mechanisms per se, realizing that a more fundamental understanding comes only with a detailed consideration of the mechanisms of the various occurring reactions.

This report is a brief summary of the present knowledge of reaction mechanisms in radiation chemistry, especially as they apply to simple organic compounds.

Fundamental Concepts

Types of Ionizing Radiations: in radiation chemistry, the energy range of the ionizing radiation commonly begins at about 100 e.v. but most studies are made with waves and particles in the Mev region (1). These energetic particles are produced by radioactive decay or by artificial means. Table 1 lists typical radiations, their principal physical characteristics, and their sources. For purposes of orientation, it should be noted that the dissociation energy of covalent bonds is in the 3-4 electron volt range.

Initial Events: When electromagnetic radiation passes through a chemical system, we may distinguish three different phenomena which govern the behavior of photons: the photoelectric effect, the Compton effect, and pair production. Figure 1 is a pictorial description of these interactions.

1. At low energies, the most important process is the photoelectric effect. In this process, a photon of energy $h\nu$ ejects a bound electron, (usually from an inner shell) from an atom or molecule and imparts an energy $h\nu - E$, where E is the binding energy of the electron. The quantum of radiation completely disappears in this encounter which is unimportant at energies above 1 Mev.

2. At exceedingly high energies, the photon is again completely absorbed in producing a positive - negative electron pair (pair production) this process is of no significance in radiation chemistry.

3. An important mode of interaction is Compton scattering. In this encounter, the photon transfers only part of its energy to a bound electron (usually an outer shell electron). The gamma rays are thus degraded and deflected. In the energy ranges most commonly used in radiation chemistry studies, and in particular for materials with low atomic numbers such as organic compounds, gamma rays lose most of their energy by the Compton scattering process.

The primary effect of a single gamma ray then may be the production of a highly energetic electron and a positively-charged ion-radical, so called because of its charge and its unpaired electron. At 1 Mev incident energy, essentially all of the electrons may be considered as of the Compton recoil type and the average energy of each electron approaches half that of the incident γ -ray (2).

Such a high energy electron can in turn produce about 20,000 additional ionizations and 30,000 excitations. This leads to the well known phenomenon that the primary events, and often the outcome of many radiation-chemical reactions, are not appreciably affected by the nature of the incident radiation.

Except for the uncharged neutrons, the other principal radiations in radiation chemistry are the alpha particles, the beta particles, and the artificially accelerated charged particles. Therefore, in radiation chemistry our attention should be directed primarily to the effects of charged particles on matter.

Energy Distribution: When a highly energetic electron, proton, alpha or other charged particle passes through a chemical system, it produces excitation and ionization events of the type illustrated in figure 2. The sequence of events is as follows:

Block I. The particle approaches five molecules; the small circles represent electrons.

Block II. The particle disturbs the electrons in some of the molecules.

Block III. The particle has traversed the fifth molecule.

Block IV. The particle has receded, leaving one molecule ionized and two in an excited state. The other molecules have reverted to the original state. The energetic electrons released from the impact process in block IV will continue to induce excitation and ionization processes at an average ratio of 2 to 1, as shown in figure 3. These "hot spots" of ionization and excitation are called clusters or spurs. The volume occupied by these clusters in a liquid has been estimated at an average diameter of 5 \AA ($5 \times 10^{-8} \text{ cm}$) (1). The distance between spurs can vary anywhere between 4600 \AA for 450 Kev electrons to approximately 9 \AA for 6 Mev alpha particles in water.

Geometrical factors are also important. Heavy particles such as alpha particles, protons, deuterons, etc., have the greatest probability of interaction with matter. However, the amount of energy is very limited. Classically, the maximum energy transferable is given by

$$E_{\text{MAX}} = E_{\text{INITIAL}} \frac{4m}{M} \quad (1)$$

where m is the mass of an electron and M is the mass of the charged particle. Thus, for alpha particles, the maximum energy transferable per collision is, classically, only $\frac{1}{1836}$ (from table 1: $\frac{4(1)}{7299}$) of the heavy particle energy. As a result of this combination of high interaction probability and low energy transfer, heavy charged particles form a very dense track of ionized and excited molecules and low energy electrons.

The probability of interaction of electrons with matter is approximately 1,000 times lower than the probability for alpha particles of the same energy. On the other hand an electron can, though relatively rarely, lose up to one half of its energy to a secondary electron. When such a large energy transfer occurs, the path of the electron will be abruptly deflected. As a result, electrons form a much less dense and zig-zagged track. Electromagnetic radiations, X and γ rays, penetrate matter for great distances before they interact with a target molecule or atom to lose all or a large part of their energy in a single event. The interaction results in the ejection of a highly energetic Compton or photo electron which traces its own characteristic trail. Hence, depending on the type of radiation used and the state of the absorbing medium, various tracks are formed which can lead to different chemical results.

Effect of Phase: The distribution of the radiation induced transient species formed along the track of a charged particle will be determined by the linear energy transfer ($-dE/dx$) appropriate to the radiation and the electron density of the medium. The life span and ultimate fate of a molecule activated by radiation may depend on whether it is in a gas, a liquid, or a solid.

1. **Gas Phase:** In the gaseous state, the parent cation is often not neutralized by recombination with its daughter electron because the low density of the medium and the absence of a solvent "cage" allows the electron to maneuver away from the parent ion's sphere of influence (Coulomb attraction). Also, both the mean free path and the average "between-collision" time are relatively large; therefore, excited molecules and ions may exist long enough to react with other transient species or to undergo unimolecular decomposition. Two radicals or ions formed by dissociation of a molecule, have a negligible chance of undergoing primary recombination and usually diffuse apart to react with other fragments. In the gas phase, there is little doubt that ion-molecule reactions are important since in many cases they appear to be a significant, and many times the dominant mechanism of chemical change.

2. **Liquid Phase:** Molecules in a condensed system are intensely influenced by neighboring molecules. Consequently the modes of energy transfer and dissociation are different. In the liquid phase, the Compton electron very often returns to its companion ion within 10^{-15} seconds, before any gross movement of molecules can occur. The attendant charge neutralization process results in the deposition of a large excess of energy within the molecule. If reionization does not occur, the highly excited molecule will usually decompose to form electrically neutral fragments or free radicals. Evidence exists that upon excitation and dissociation, the weakest bond is likely to break, with the excess energy distributed as kinetic energy between the recoil species. The free radicals thus formed are usually surrounded by a "cage" of solvent molecules which hinders their diffusion outside the cage. The result is that the radicals lose their energy by colliding with the cage "walls" and immediately recombine. The probability of such deactivation and recombination decreases if one of the radicals is small. This effect, usually called the Franck-Rabinowitch Cage Effect, operates to decrease yield in liquids when the decomposition proceeds via free radical decomposition.

3. Solid Phase: In the solid state, diffusion is an extremely slow process which gives rise to product localization for measurable periods of time. Also, as the result of the systematic arrangement of molecules in crystals, radicals may preferentially attack certain portions of adjacent molecules rather than attack randomly as in the liquid or gas phase. Most organic solids are covalent and localized damage is often subsidiary to the formation of free radicals and molecular products, both of which would be trapped. Fusion of the solid allows the trapped volatile molecular products to escape thereby releasing the free radicals from their position within the lattice and enabling them to react or undergo mutual destruction.

These differences in the state of aggregation of the absorbing or "target" medium often create differences in the nature and yields of radiolytic products. At present, neither the phase effect nor the theory of radiation induced reaction mechanisms are established well enough to allow reliable predictions of the extent the phase will influence the products of a given radiation chemical reaction.

Molecule Activation In a Radiation Field

We have seen that when a charged particle traverses matter, it produces a number of active species of greater-than-average energy. These ephemeral species may revert to their original inactive form or, they may react with neighboring molecules before deactivation. The time it takes for the activated species to become deactivated usually determines their chemical reactivity. If they were completely isolated in space, many ions and radicals would be stable indefinitely. Actually, these "unstable" entities have a fleeting existence only because a more stable situation can be established by interaction with an adjacent molecule or ion.

Excited Species: It has already been stated that in radiation chemistry, there are 1.5 to 2 excited molecules formed per ion pair. For most gases the energy required to form an ion pair, W , is about 30 electron-volts (ev). W is not known for liquids however. Since the ionization potential, I , for most gases is about 10-15 ev, then 15 to 20 ev of absorbed energy must go into electronic excitations. Moreover, many ion-pairs formed in a radiation-chemical process recombine to generate highly excited molecules. This means that the total number of excited species produced by high energy radiation is even greater than expected from ion-pair estimates.

Molecules with excited electrons are usually unstable even if isolated in space. They may be produced directly in an initial event or as a result of an ion recombination reaction. Direct excitation usually results in elevation to low excited states. Since the ground state of most molecules is singlet (no unpaired electrons), the more easily excitable states will also be singlets i.e., ones in which the electrons are still paired although the excited electron is now in a more distant spatial orbit. However, in radiation-chemical reactions triplet states often play an important role. A triplet state can be defined as bond excitation where one of the bonded electrons is excited into a higher energy level with reverse spin. Generally, low triplet states do not possess enough energy to break a covalent bond. Since most upper excited states internally convert in a very short time to the lowest excited states of the same multiplicity, and since internal conversion to the ground state is much slower, most of the chemical changes occur from either one of the two low excited states (3).

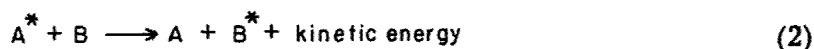
Figure 4 is a schematic diagram of the lowest important electronic energy levels of a molecule. The diagram depicts two systems of levels, the singlet system (S_0, S_1, S_2) and the triplet system (T_1, T_2). Excitation of the molecule occurs by absorption of radiation

which raises the molecule from the ground state (S_0) to elevated singlet or triplet stages. The transition $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ are usually photochemically forbidden and the photochemical absorption processes are usually inefficient and therefore ignored. In radiation chemistry, however, triplets can be formed directly and by ion neutralization as well as by $S \rightarrow T$ transitions; therefore, the relative triplet/singlet yield ratio would be expected to be much higher in radiation chemistry. After excitation to S_1 , the molecule can be deactivated in three ways: 1. by fluorescence, a radiative decay to the ground state (F); 2. by quenching a radiationless decay whereby the excitation energy is converted to thermal energy (Q); 3. by a radiationless internal conversion to a triplet state (C_i). Once the molecule occupies the T_1 level it can either phosphoresce (P) to the ground state or it can be quenched (Q) nonradiatively. If the molecule is initially excited to a higher singlet level (S_2) it usually becomes "degraded" via two alternative paths: a) by an internal conversion (C_i) to a lower-lying singlet level ($S_2 \rightarrow S_1$); b) by an internal conversion (C_i) to a triplet level.

Phosphorescence usually involves the lowest triplet state while fluorescence usually occurs from the lowest excited singlet state to the ground state which is the lowest singlet state. The reason that only the last step is a radiative one is that the largest energy gap is usually between the ground and the first excited states so that the necessary overlapping of potential energy surfaces required for a radiationless transition is less likely between these two than between closer lying pairs (2).

Excluding collisional deactivation and including the aforementioned processes, the following is a list of the more important processes by which an excited molecule can become deactivated:

- 1) Internal conversion to lower excited levels.
- 2) Internal conversion to the ground state.
- 3) Emission of energy as luminescence (fluorescence and/or phosphorescence).
- 4) Energy transfer, for example



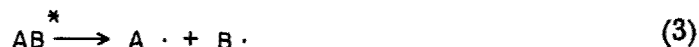
Aromatic and phenylated compounds function very effectively as the molecule B. Such compounds afford protection by absorbing energy from the more sensitive and excited (*) molecule A and dissipate most of it without decomposition. If the additive B protects A by dampening any luminescent effect from A the method of protection is called "quenching"

5) Stern-Volmer Reactions - complicated reactions involving one or more excited molecules.

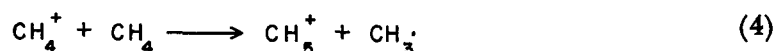
- 6) Decomposition reactions leading to molecule or free radical formation.

Free Radicals: The free radicals found in a radiation-chemical process are the products and by-products of the following reactions:

1. Decomposition of excited molecules



2. Ion-molecule reactions; a specific example is



3. Ion-formation (dissociative electron capture)



4. Ion neutralization (dissociative recombination)

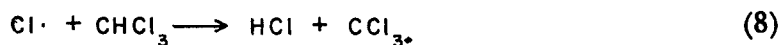


Most of the above reactions will take place in a spur or ion track within 10^{-11} seconds. It is generally agreed that in a radiation-chemical process within a condensed system there exists initially high concentrations of free radicals in spurs or clusters. The number of isolated radicals is believed to be small, even in fast particle tracks. The distribution of radicals in a track will be determined by the Linear Energy Transfer (LET) of the radiation in question and the electron density of the absorbing medium. The concentration will tend to become uniform by diffusion. In liquids this diffusion process is hindered by the Franck-Rabinowitch Cage Effect. According to this principle, a pair of radicals surrounded by a "Cage" of solvent molecules may lose energy and recombine before the moieties leave each other's sphere of influence. The "Cage" therefore protects a molecule from dissociation into free radicals. The cage effect therefore operates to decrease the yield in liquid systems when the decomposition is through a free radical process. Once the free radicals diffuse out of the cage their probability of returning and undergoing a secondary recombination is usually very low. Escape therefore allows the radicals the freedom to undergo characteristic free radical reactions such as the following:

1. Radical Displacement



This type of reaction has been used by countless workers to explain radiation induced reactions, e.g., Stein, et. al. (4), explained the formation of HCl in the radiolysis of chloroform with the following reaction.



2. Radical Addition



Free radicals characteristically attack the π electrons of unsaturated compounds to form new radicals such as $\text{AB}\cdot$. Reaction (9) has been shown to be very important in radiation-induced polymerization reactions.

3. Radical Coupling



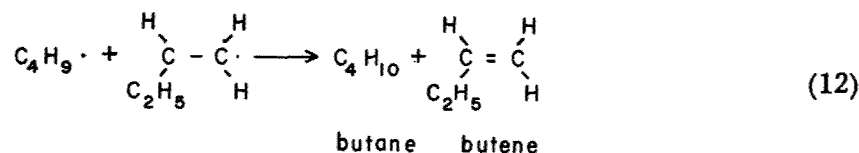
Radical combination or coupling is different from radical recombination to the extent that the latter occurs primarily within the solvent cage. Radical combination is the reverse of the homolytic dissociation of a covalent bond. The activation energy for such

reactions is usually zero while the rapidity is very great. For example, in the gas phase, methyl radicals combine at almost every collision to form ethane. Kerr and Trotman-Dickenson (5) extended their study to the combination of unlike radicals and have found that combination also occurs at every collision in the gas phase. The speed of coupling in the liquid phase is usually slower and the rates of radical coupling reactions usually do not vary far from the velocity of diffusion.

4. Radical Disproportionation



Despite the rapidity of radical combinations, a competing reaction is that of disproportionation into a saturated (AH) and unsaturated (U) molecule. The difference between coupling and disproportionation can be explained in terms of the mode of encounter of the free radicals (6). A head-to-head encounter of radicals A' and B usually results in the formation of one molecule while a head-to-tail encounter sometimes results in the abstraction of hydrogen atom from one radical by the other and the formation of one saturated and one unsaturated molecule; for example:

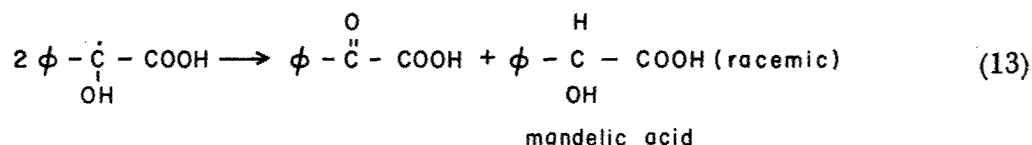


Activation energies for disproportionation are very close to zero and Wagner (7) has observed that such reactions should be important in gas phase radiolyses.

5. Radical Rearrangements or Isomerizations

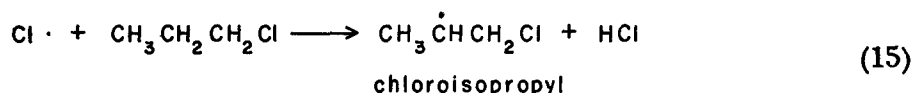
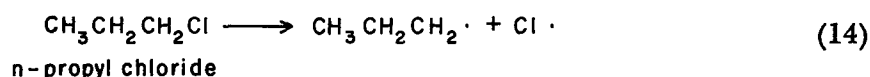
Two types of isomerizations must be considered: the racemization of optically active compounds and the rearrangement of bonds within a radical.

In a study made by Feng and Tobey (8) on the gamma radiolysis of aqueous solutions of mandelic acid, racemization and destruction of the asymmetric center were found to occur. This reaction



was advanced to explain the observed extent of radiation-induced reaction in optical activity.

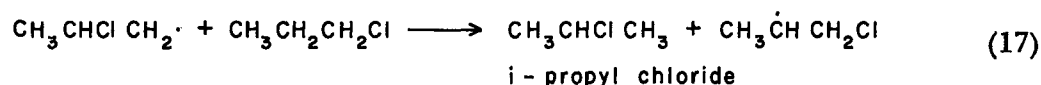
A free radical mechanism has been used also to explain the gamma-radiation induced isomerization of normal-propyl chloride to isopropyl chloride (9). The following sequence of free radical reactions were presented:



It was then suggested that the chlorine atom in the chloroisopropyl radical migrates to the β -position,



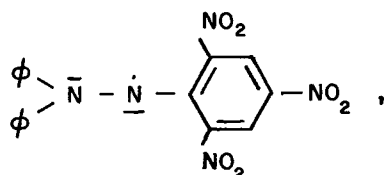
followed by hydrogen abstraction by the chloropropyl radical



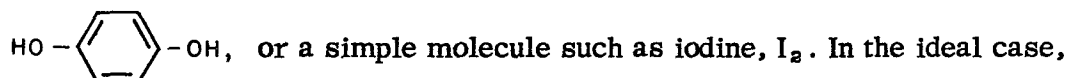
6. Free Radical Scavenging



Reaction (18) represents the closest approach to a basic study of free radicals in radiation chemistry. It entails the use of a radical trap or scavenger, S, which may be a stable free radical such as diphenylpicrylhydrazyl,



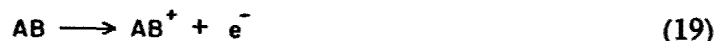
a complex molecule such as hydroquinone,



reaction (18) must take place before any of the aforementioned free radical reactions. Reaction (10), the coupling of various free radicals to form the original irradiated substance, may be faster than reaction (18), however, this is due primarily to the Franck-Rabinowitch Cage Effect. Scavengers would not be effective in removing radicals until after they had diffused out of this cage (10). Since recombinations within the cage do not enter into the chemical picture and since the object of the scavenger addition is to determine the overall free radical yields, no appreciable error is introduced by disregarding the radicals involved in such a recombination. The possibility exists however, that under different physical conditions the rates of the recombination and scavenging reactions might be sufficiently different and result in different radical yield. For example, a variation in temperature may affect the diffusion rates in such a way that the free radicals within the cage may be separated from each other in a shorter time than it takes for the recombination to occur.

One of the problems which arises when "scavengers" are used to determine the nature of radiation-induced free radicals is that some scavengers appear to react with excited molecules with the formation of products exactly like those formed from free radicals. Therefore, whenever information is given about free radicals yields from scavenger-type reactions, the data should be carefully analyzed before false conclusions are drawn.

Ion-Radicals: In the reaction

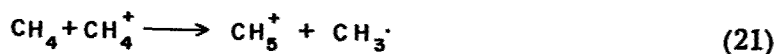


the species AB^+ should not be mistaken for an organic "onium" -type ion because the latter has no unpaired electrons; neither can it be regarded as a free radical since it is positively charged. Because of their charge and the unpaired electron, these bifunctional species have been called ion-radicals. Their existence in the liquid phase is improbable; however, they are produced to some extent in the gas phase and hence, their presence cannot be completely ignored. A mass spectrometer study has called attention to some of the similarities of free radicals and ion-radicals. Three general ion-radical reactions, similar to the general processes known for free radicals were examined.

1. Ion-radical displacement



An analysis of rate constants reveals that ions undergo displacements from 10^3 to 10^5 times faster than free radicals. The reaction is analogous to the well known ion-molecule reaction

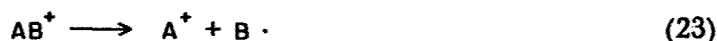


2. Ion radical addition



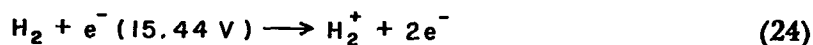
This reaction perpetuates ion radicals in the same way that growing free radical polymer chains are formed.

3. Ion-radical decomposition

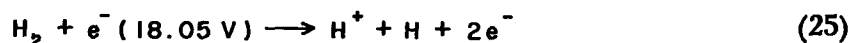


These decompositions result in the formation of many metastable ions observed in mass spectra. Ionic reactions of this type produce free radicals and/or ion radicals. This process is another example of the close relationship between ion-radicals and free radicals.

Ion-Molecule Reactions: Most of the information concerning ion-molecule reactions has been derived from mass spectrometry. Since at 10^{-6} mm pressure in the ionization chamber of the mass spectrometer the mean free path of a molecule is $\sim 10^4$ cm, collisions between molecules and ions are rare and the ions are formed by unimolecular decomposition as a result of direct impact of electrons on the molecular beam. The smallest voltage required to energize the electrons sufficiently to remove an electron from a molecule is its ionizing potential (IP) and is 15.44 V for hydrogen.



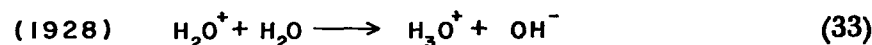
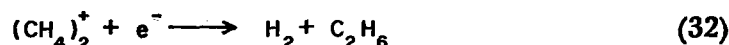
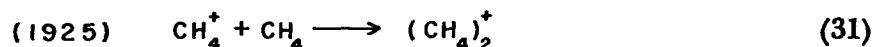
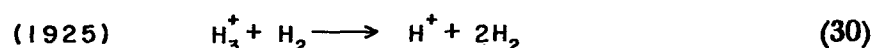
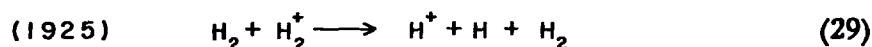
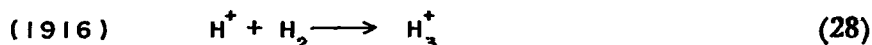
Still more highly energized electrons may cause the molecule to fragment. This necessary voltage is called the appearance potential (AP) and is 18.05V.



The energy of fragmenting can be calculated from Hess's law if we make a summation of the processes:

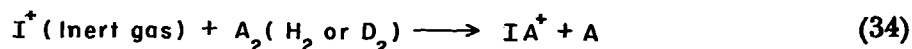


Since most ion-molecules are short-lived, many ions which are formed and disappear in less than 10^{-8} seconds cannot be detected by the mass spectrometer. Some early observed ion molecule reactions (12-15) are:



A number of recently discovered ion molecule reactions are tabulated in a review by Lampe and Field (16).

A most interesting positive ion formation for neon, argon, and krypton has also been observed. These positive ions can react with hydrogen or deuterium



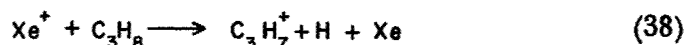
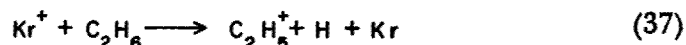
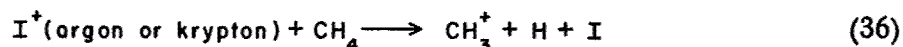
A variety of both organic and inorganic ion molecule reactions have been identified by the mass spectrometer. Perhaps one of the most unusual species was the identification of CH_6^+ from the following:



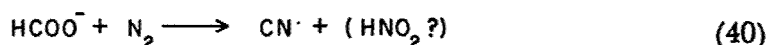
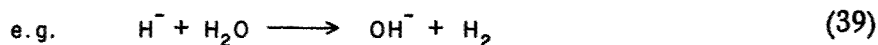
In all these reactions the atom transferred was either positively charged or neutral. The reaction involving the transfer of a proton occurs much more readily than that which involves the transfer of a hydrogen atom.

Although the transfer of a hydride ion had been postulated for many years as one of intermediates in an ion molecule reaction, direct observations were first made in the gas

phase by Lampe and Field in 1958 (17) and are tabulated on page 200 of reference (16). The reaction observed by Meisel et. al. (18) constitutes another example in which the loss of a hydride could account for the changes indicated.

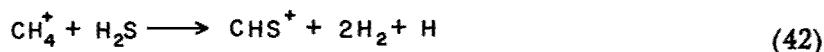


There are two more classes of ion molecule reactions. One is the negative ion reactions about which very little is known:



The above two examples are the only ones we have found.

The second class of ion molecule reactions are of the condensation type. Here a good deal more is involved than the transfer of an atom or atomic ion.



These and a number of other examples are listed on page 202 of reference (16).

The description of ion molecules observed in the mass spectrometer may easily be extrapolated to an environment subjected to ionizing radiation when the electron, just as in the mass spectrometer, is responsible for the overwhelming number of events. Hence, the information presented must be regarded as a potential mechanism of reactions characteristic of molecules in a radiation environment.

Past, Present, And Future Applications

Since a molecule may break in various ways, the complexity of products resulting from these interacting fragments is very great. In addition, the effect of state introduces still another variable. These factors require clarification to understand better the role of ionizing radiation. The problem becomes still more complicated if these studies are conducted in a hard vacuum simulating a space environment. It is in these areas where a variety of basic problems exist and study is necessary. As an example, a very important area for investigation in view of current trends appears to be a study of the effects of ionizing radiation on propellants - both liquid and solid. It is anticipated that chemical propellants may be exposed to the space radiation environment for long periods before being subsequently used for retro, maneuver, or primary propulsion as with a satellite launched missile. Will prolonged exposure bring about chemical changes in the propellant which would impair the operational reliability of the vehicle? For some missions the rocket casing or vehicle shell may be sufficient shield against potentially damaging radiation; for other missions this may not be true. On the other hand, perhaps the effect

of ionizing radiation could be beneficial by using a liquid propellant which would subsequently be changed through exposure to a solid in which form it would be used.

Another concept which might be explored for space applications is the use of a material in a radiation field to serve one function for a limited time and a second function after it has been altered by the ionizing radiation. The potential use of some liquid propellant for shielding and its subsequent use as a solid propellant would be an example of this concept. Or possibly some shielding liquid which would be converted by ionizing radiation to the consistency of a lubricant could be used for such a double duty application.

Radiation chemistry has been disappointing since we have not been able to use it as a catalyst to produce desirable chemical products otherwise not available by conventional means. Although a few such applications are known, a great deal remains to be done in this field - in particular for the development of radiation stable materials. It would be very likely that materials prepared in this way would have passed part of the test for radiation stable materials in their very formation. The preparation of useful ferrocene polymers by irradiating di- and poly-halo ferrocenes appears to be a possible application of this concept. The horizons here are limited only by the imagination of the synthetic chemist. The use of radiation as a catalyst has the unique feature of not requiring the presence of foreign chemicals as is the case with conventional catalysts. Some known examples of chemical changes induced by radiation are the formation of lindane from benzene and chlorine; phenol from water, benzene, and oxygen; ethylene glycol from methanol; aniline from benzene and ammonia; fixation of nitrogen; alkyl sulfonates from hydrocarbons and sulfur trioxide; formation of ascorbic acid and many others.

A great deal of work remains to be done to understand what makes a molecule radiation stable. Many empiric generalizations have appeared in this field, but these fall or are restricted as new cases are discovered. Some work is being done to show the mode of energy transfer from less to more stable molecules. In our laboratory some radiation resistant alkynes have been found to exist although this was not anticipated from the known high reactivity of acetylene itself under ionizing radiation. Rather than accept these results as the fruits of serendipity it is believed a better understanding of radiation stability is required. The ripe possibility exists for obtaining such information as well as useful new materials for a radiation environment if the general area of aromatic compounds are studied in particular, the conjugated cyclic organic compounds having alternating single and double bonds which comply with Huckels rule. Investigations should include studies of stability of molecules ranging from cyclopropene to macrocyclic molecules with 5, 7, 9, and 11 bonds, e.g. the phthalocyanines and porphyrins.

The ever present requirements of dosimetry exist in both the laboratory and in the field. Although heavy inroads have been made in this area there is ample need for new concepts of dosimetry - physical or chemical. In the liquid phase ceric sulfate, ferrous sulfate, and cyclohexane are commonly used dosimeters, while in the gas phase the most commonly used dosimeter is acetylene. There is some doubt that acetylene is a reliable dosimeter (19). A need exists for the development of an improved gas phase dosimeter. This is especially important since the research in radiation chemistry is heavily dependent upon dosimetry. In the chemical area limited amounts of work has been done on the effect of radiation on optically active molecules. Surely there are a host of other more ingenious approaches to find new concepts and compounds useful in dosimetry. This will no doubt evolve in a better understanding of radiation chemical phenomena. Surely in these and related studies radiation chemistry has found a host of applications.

Some idea of the future of radiation chemistry may be gained from a brief resumé of past accomplishments in the field. A few of the more important examples are: Sterilizing

of heat sensitive products such as, maturing of fruits, wines, liquors, and cheese; production of static free fibers; cross-linking of polymers; vulcanization of rubber without sulfur; syntheses of a new chemicals; grafting of incompatible polymers such as, nylon and cellulose; dying teflon; initiating reactions at low temperatures; and the mutation of plants.

The future application arising from a better understanding of radiation will certainly far exceed these past developments. Foresight on the part of management and the research scientist will be required to anticipate many of these needs by entering the field now and developing the required capability.

V. BIBLIOGRAPHY

1. M. Burton, Record of Chemical Progress, 19, 13 (1958)
2. C. Reid, "Excited States in Chemistry and Biology", Academic Press, (1959)
3. M. Burton, W. Hamill, and J. Magee, Second UN Geneva Conference on Peaceful Uses of Atomic Energy, 29, 391 (1958)
4. G. Stein, M. Ottolenghi, and I. Eliezer, WADD Technical Report 60-668 (1960)
5. J. A. Kerr and A. F. Trotman - Dickenson, Chemistry and Industry 125 (1959)
6. A. F. Trotman-Dickenson, "Free Radicals", John Wiley & Sons, Inc. (1959)
7. C. D. Wagner, Journal of Physical Chemistry, 64, 231 (1960)
8. P.Y. Feng and S.W. Tobey, Journal of Physical Chemistry, 63, 759 (1959)
9. R. H. Wiley, W. Miller, C. Jarboe, J. Harrell and D. Parish, Radiation Research, 13, 479 (1960)
10. R. Britton and I. Zwiebel, WADD Technical Report 60-127 (1960)
11. T. W. Martin and C. E. Melton, Journal of Chemical Physics, 32, 700 (1960)
12. A. J. Dempster, Phil. Mag., 31, 438-43 (1916)
13. H. D. Smyth, Phys. Rev., 25, 455 (1925)
14. S. C. Lind, D. C. Bardwell, Science, 62, 422-24 (1925)
15. H. A. Barton, J. H. Barlett, Jr., Phys. Rev. 31, 822-6 (1928)
16. F. W. Lampe, F. H. Field, Tetrahedron 7, 196 (1959)
17. F. H. Field, F. W. Lampe, J. Am. Chem. Soc. 80, 5587 (1958)
18. G. G. Meisels, W. H. Hamill, R. R. Williams, Jr., J. Chem. Phys. 25, 790 (1956);
ibid. 61, 1456 (1957)
19. H. A. Samuel, private communication

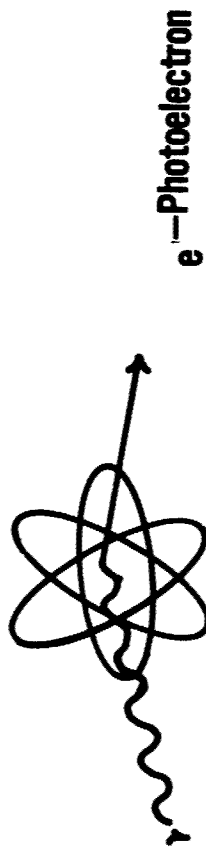
TABLE I
PRINCIPAL FORMS OF IONIZING RADIATION

RADIATION	SYMBOL	RELATIVE MASS	CHARGE	SOURCE
ELECTRON	e or e^-	1	-	NATURAL AND ACTIVATED RADIO - NUCLIDES, PARTICLE ACCELERATORS
PROTON	H^+	1836	+	PARTICLE ACCELERATORS
NEUTRON	n^0	1839	0	REACTOR FISSION PRODUCTS
DEUTERON	D^+	3671	+	PARTICLE ACCELERATOR
HELIUM NUCLEUS	He^{++} or α	7296	++	NATURAL RADIO - NUCLIDES, PARTICLE ACCELERATORS
ELECTRO-MAGNETIC	X and γ	0	0	NATURAL AND ACTIVATED RADIO - NUCLIDES, FISSION PRODUCTS, AND ACCELERATOR TARGETS

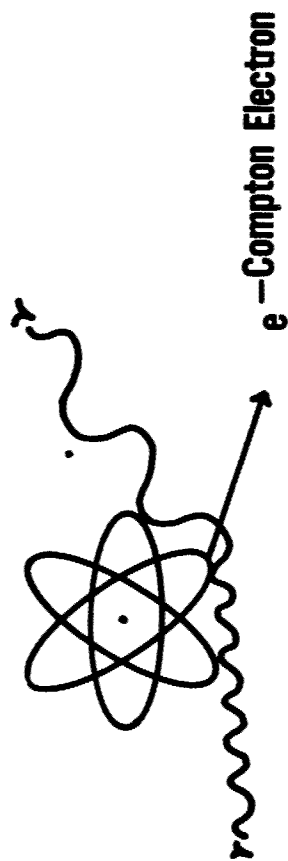
X-RAY INTERACTIONS

Atom Or Molecule

Photoelectric Effect



Compton Scattering



Pair Production

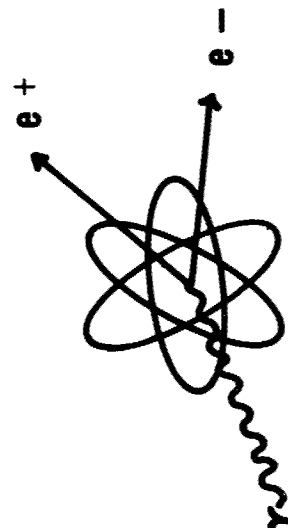


Figure 1.

PRIMARY EFFECTS

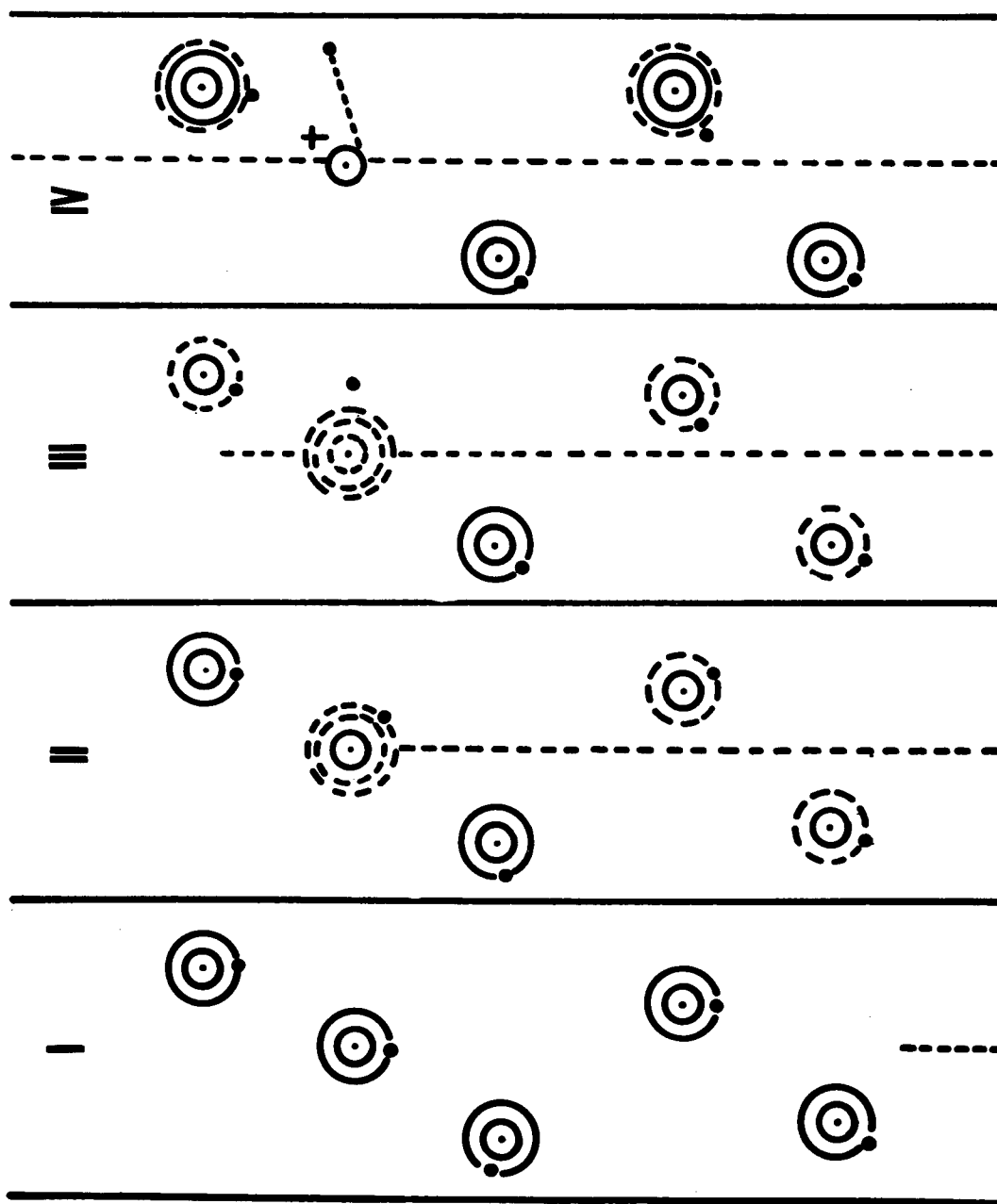


Figure 2.

SPUR FORMATION

⊙ + Ionized
⊙ Excited

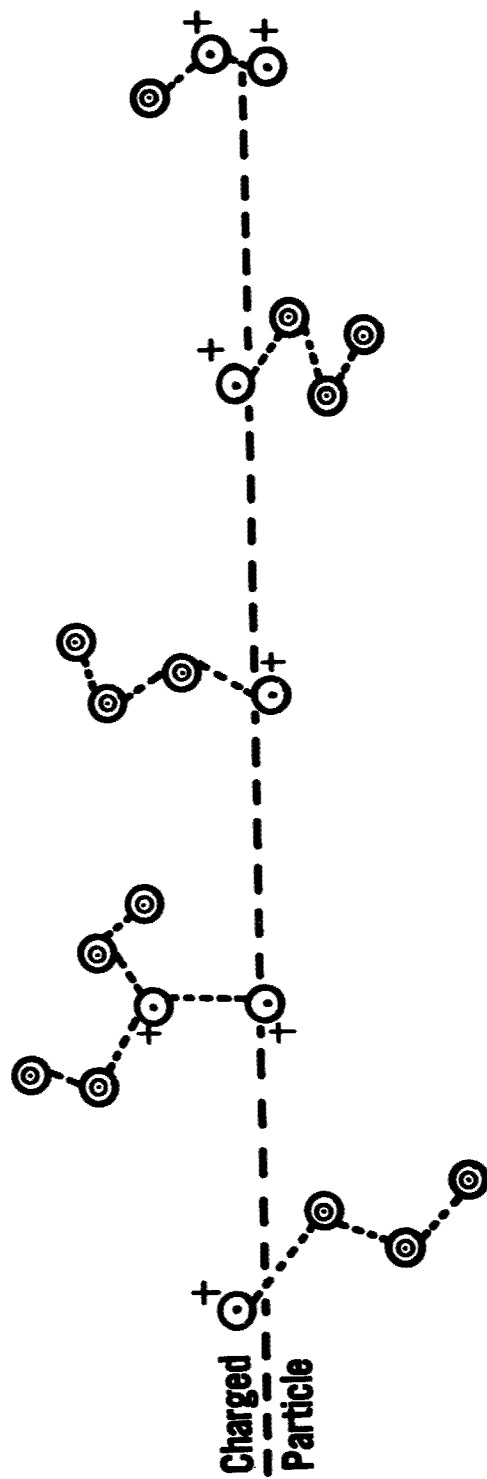


Figure 3.

EXCITED STATE ENERGY DIAGRAM

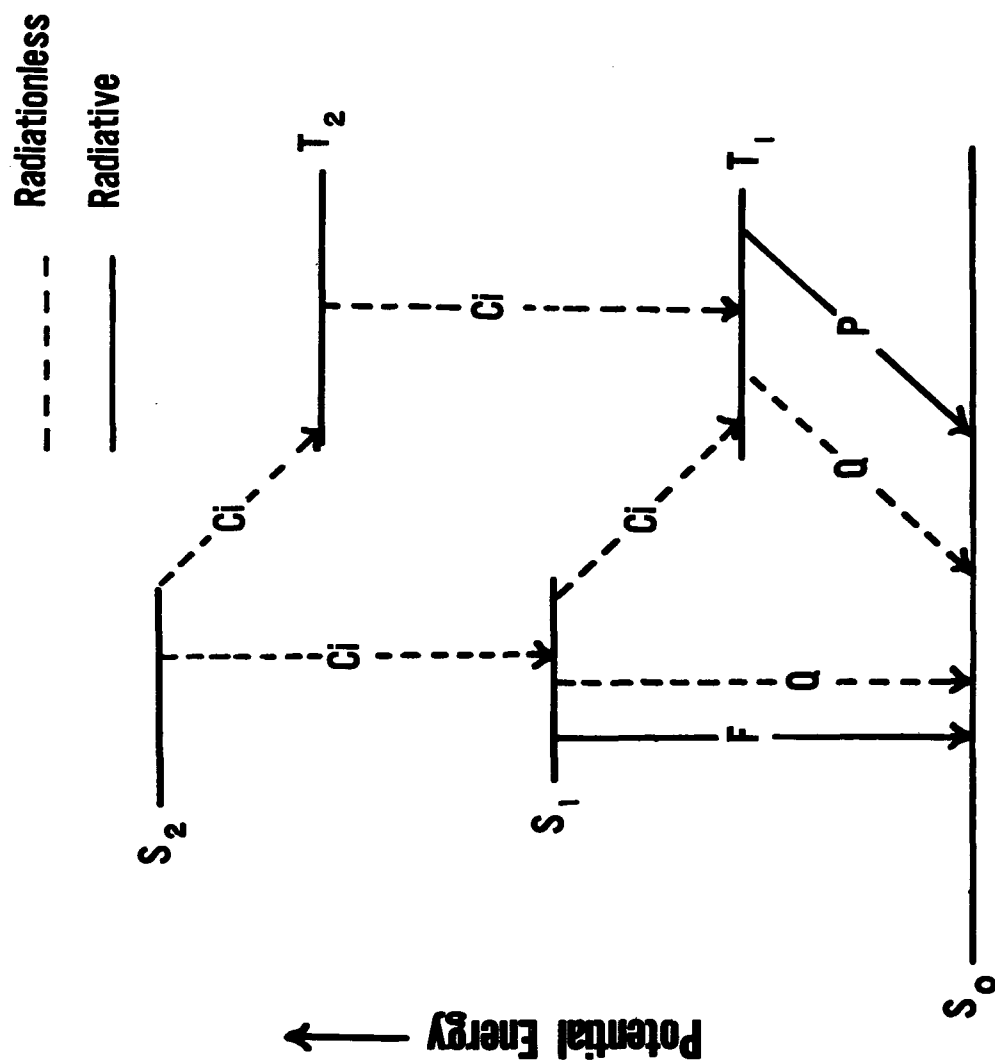


Figure 4.

RADIATION EFFECTS ON MATERIALS IN SPACE

R. L. Hickmott
G. H. Griffith
V. L. Donlan
O. V. P. Sessoms
T. W. Bailey

Directorate of Materials and Processes, ASD

Introduction

Both manned and unmanned vehicles will be needed for Air Force missions in space. This paper sketches the radiation effects situation to be expected. The treatment is general and qualitative with no effort to present detailed, quantitative data.

There are two types of radiation to consider: man made radiation due to reactors, and natural radiations in space. These will be discussed separately here, though in the area of personnel shielding at least, they should probably be treated together.

Reactor Radiations

Currently, solar cells and chemical batteries provide all the auxiliary power used by space vehicles. Their limitations are well known. (1) Batteries suffer from limited life unless recharged by devices like solar cells. Solar cells have a low power output that diminishes as the vehicle recedes from the sun. The SNAP (System for Nuclear Auxiliary Power) program of the AEC is set up to overcome these limitations by using radioisotopes and nuclear reactors to generate auxiliary power. Odd-numbered SNAP's use the heat from radioisotopes to generate electricity; even-numbered SNAP's use nuclear reactors as energy sources. These two types of energy source supplement each other. Radioactive isotopes may be used up to a few thousand watts, while nuclear reactors may be used from there on up into the megawatt range (1,2). This paper is not concerned with the design problems of SNAP generators but rather with their leakage radiation and its effect on materials.

Sufficient shield weight can reduce the leakage radiation to any value desired; however, because of the weight penalty the design leakage radiation will have to be as large as can be tolerated to save shield weight. Since the leakage radiation in unmanned vehicles will be determined by the radiation tolerance of its materials and components, these will have to be designed for maximum radiation resistance.

As an example of the leakage radiation to expect from an isotope powered SNAP, consider the SNAP 1A (3). This unit is designed to furnish 125 watts of electrical power for about one year. It is fueled with 8.8×10^5 curies of radioactive cerium with a 285 day half life, and its weight is about two hundred pounds. Radioactive cerium decays by beta emission which is easy to shield. However, there is also considerable gamma ray emission associated with the cerium and its daughter products. Accordingly, SNAP 1A is shielded for ground handling by four thousand pounds of mercury which reduces the leakage radiation at three feet to less than one tenth roentgen per hour (4). The mercury is drained out before space flight. Without the mercury the resulting dose rate at three feet is expected to be 20,000 roentgens per hour, which over a period of a year results in a total exposure dose of about 10^8 roentgens. Organic materials and solid state electronics are disturbed

by doses this large. There are plans to scale up the power from approximately 100 watts to perhaps twenty kilowatts which could increase the radiation dose rates by a factor of one hundred or so, demanding more severe requirements on materials and components.

SNAP's powered by nuclear reactors are proposed to handle power requirements in the range of one hundred kilowatts and up (2). SNAP 8, for example, is a low power reactor to provide thirty kilowatts of electricity. The leakage radiation through the four hundred pound shadow shield is expected to be a dose rate of about 1000 roentgens per hour of gammas and a fast neutron flux of 30,000 neutrons per cm^2/sec^2 . Again, the allowable leakage radiation in unmanned vehicles will be determined by the radiation tolerances of materials and equipment. There is a lot of radiation effects data available in this connection but it does not apply across the board in the vacuum of space.

Low power SNAP's will probably be used only on unmanned vehicles where the leakage flux will be limited by the radiation sensitivity of materials and components. On the other hand, power SNAP's (one hundred kilowatts and up) have application to manned vehicles also. Man is thousands of times more radiation sensitive than is any inanimate object in a space vehicle and the problem of shielding-weight increases in proportion in a manned vehicle. Interplanetary travel by ion propulsion will require megawatts of power and presumably these missions will eventually be done in manned vehicles. The nuclear rocket (Rover) is talked of in terms of hundreds or even thousands of megawatts. What must be done to shield crew members from these reactor radiations? The fact that the vehicle will be surrounded by a vacuum in outer space rather than by air, which would back scatter the radiation, should simplify the shielding design. Weight savings should result from shadow shields designed to scatter radiation into space instead of relying exclusively on absorption (5). Even so, it appears that considerable shield weight will be needed for personnel in vehicles using high power reactors. The most efficient position for scatter shielding is probably close to the reactor where smaller angle scattering can deflect the radiation from the solid angle subtended by the crew compartment. Nevertheless, if protection from the natural radiations in space is considered at the same time, it may be well to put a disproportionately large fraction of the shield weight at the crew compartment so that if the natural radiations from space build up, the crew can shut down the reactor and retire into the crew compartment part of the divided shield for protection.

Both neutrons and gammas are scattered most efficiently (on a weight basis) by low atomic number materials, particularly hydrogen. Light metal hydrides and organic materials rich in hydrogen are candidate materials for scatter shields.

Another method for shielding in space is $1/R^2$ shielding; simply putting the crew compartment as far as possible from the reactor. This is feasible because stresses due to gravity are much reduced in space so that the power source can be separated by a considerable distance from the equipment it operates and can be connected by relatively long, light conduits.

Natural Space Radiations

The following natural space radiations are considered: galactic cosmic rays, solar cosmic rays, Van Allen radiation belt electrons, and Van Allen radiation belt protons.

Conventional Shielding

Space radiation fluxes are much less than those of nuclear reactors but their effects are less well known. In addition they affect all space missions including those that do not

involve nuclear power (6). Some of the results and conclusions that follow are based on our calculations. The differential spectra used are questionable, particularly the spectrum of the Van Allen radiation belt electrons which is not well known. However, the conclusions are qualitative and are not greatly dependent on the particular spectra chosen.

Cosmic rays have been studied extensively (7). Galactic cosmic rays originate outside the solar system and seem to permeate the vacuum of space. Their composition is quite well known, mostly protons with a smattering of heavier elements. Conventional shielding probably cannot shield the primaries effectively. Fortunately the dose rate expected from them in space is only about 0.001 roentgen per hour (6) which could be considered negligible except for uncertainty about the biological effects of the high atomic number component of the radiation. Galactic cosmic rays will not be considered further here.

Solar cosmic rays are bursts of high energy protons associated with flares on the surface of the sun. These bursts last a few hours, decaying as the square of the time. Solar cosmic ray bursts are classified as high energy events or low energy events. Their occurrence is unpredictable.

Low energy solar cosmic ray bursts average about one a month during the active part of the eleven year solar cycle, and are less frequent during the solar minimum. They contain protons up to several hundred mev energy. A rather intense low energy cosmic ray burst occurred on 12 May 1959. Its spectrum was measured at balloon altitude (8). Proton range and energy loss data can be used with this spectrum to compute the dose to be expected. Using Sternheimer's data (9), our calculations indicate a dose of about 27 rad through $1\frac{1}{2}$ inches of aluminum (10 g/cm^2 of absorber). This small a dose would have a negligible effect on materials and could be tolerated by man. The proton spectrum is steep, making it relatively easy to shield. Nine inches of aluminum (20 g/cm^2 of absorber) would reduce the dose to 1.5 rad. Accordingly, it appears that conventional shielding can reduce to tolerable levels the radiation dose due to solar cosmic rays from low energy events.

This may also be true of solar cosmic rays from high energy events. Nevertheless, these constitute a major radiation hazard to man in space. There have been half a dozen or so high energy events since 1940 which contained protons with energies of tens of billions of electron volts. A particularly intense high energy event took place on 23 Feb 1956. We did not actually compute doses expected from this event; however, reference (6), shows 40 times as many protons able to penetrate $1\frac{1}{2}$ inches of aluminum as there were in the event of 12 May 1959. Hence, the dose should be about forty times as great or about 1000 rad. This would not significantly effect materials but would be fatal to personnel. Reference (6), also shows that about 100 times as many protons are able to penetrate 9 inches of aluminum, as there were in the event of 12 May 1959, which implies a dose of about 150 rad through a 3-inch thickness of shielding. A dose of 150 rad would not be fatal and the risk of a 100 rad dose could probably be tolerated since high energy events are so infrequent. Unfortunately, future high energy events can be expected to exceed in intensity that of 23 Feb 1956. Another disturbing feature of these events is the large flux of protons with energies above one billion electron volts. It would require five feet of structure to shield 1 Bev protons by conventional means. For this reason unconventional shielding techniques appear attractive. Furthermore the biological effects of high energy protons are not known but are probably worse than the dose in rads implies. This is also true, to a lesser extent, of their effects on materials in general.

Girdling the earth are two regions of trapped radiation called the Van Allen radiation belts (10). The inner Van Allen belt contains trapped protons and electrons; the outer Van

Allen belt primarily trapped electrons. The heart of the inner zone is about 2000 miles from the earth at the equator; the heart of the outer zone, about 10,000 miles. This paper will not discuss the shape or extent of these zones which is covered in a number of survey articles (11). Suffice it that these regions are bounded, and can either be traversed quickly or avoided altogether in some missions. There may be other missions where a vehicle must spend considerable time within them.

Treatment of the trapped protons is similar to the previous treatment of low energy solar flares except that dose rates are significant instead of total doses since the flux of trapped protons appears to be quite stable, and doesn't decay with time as does the proton flux from solar flares. The trapped protons have energies up to several hundred Mev as do the protons from low energy solar flares. However, the spectrum (12) of trapped protons is much flatter which makes it much more difficult to shield by conventional means. Our calculations show a dose rate of about 4 rad/hr through $1\frac{1}{2}$ inches of aluminum (which is comparable to the maximum dose rate from the 12 May 1959 solar flare of 27 rad/hr). However, 3 inches of aluminum, which would reduce the flare to 1.5 rad/hr, reduce the trapped protons only to 2.2 rad/hr. Again these dose rates pose minor problems for most materials but are much too high for people to loiter in.

The Van Allen Radiation belts also contain trapped electrons. One mechanism for their production is by the decay of neutrons which are generated by cosmic rays interacting with the atmosphere (13). The neutron decay is as follows:

$$n \rightarrow p + e + 754 \text{ Kev}$$

This implies that electrons are injected into the radiation belts with energies of 754 Kev or less. The fluxes of electrons in the Van Allen belts are not yet as well known as the proton fluxes but the electron fluxes appear to have an effective upper limit of around 800 Kev. These electrons can be completely stopped by a few millimeters of aluminum and will not penetrate normal satellite structure to effect directly materials or personnel. However, when electrons are stopped, bremsstrahlung are produced and the effects of these must be considered. Bremsstrahlung production varies directly with the atomic number of the material that stops the electrons. Calculations for electrons stopped in aluminum indicate dose rates of a couple rad per hour of rather soft x-rays. One tenth inch of lead can reduce this dose rate by a factor of one thousand to completely tolerable values. Bremsstrahlung production can be reduced by stopping the electrons in material of lower atomic number. Special low atomic number coatings may be worth developing if it turns out that other planets have trapped electron belts a great deal more intense than that of the earth.

Unconventional Shielding of Protons

Conventional shielding is based on protons losing energy by ionization and excitation processes. This is a reasonable way to shield against 100 Mev protons which are stopped by $1\frac{1}{2}$ inches of aluminum. There may be better ways to reduce the hazards of Bev solar flare protons which have ranges of several feet in aluminum. In addition, protons over a few hundred Mev can create unexpected and exotic secondaries, like mesons in conventional shields (1). Even low energy protons coming through a shield are a source of concern since their biological effects are not well known.

Magnetic shielding and electrostatic shielding take advantage of the charged nature of the radiation to be shielded. Magnetic shielding relies on a magnetic field of sufficient strength to deflect the protons. To produce such a field with existing technology would

require very large electric currents which are difficult to provide under present weight limitations. In addition, inherent properties of magnetic fields are such that protons coming in at the magnetic poles would be undeflected.

Electrostatic shielding appears more attractive. If a few coulombs of negative charge can be removed from a satellite, it would charge up to some billions of volts. Any proton with energy less than this would not even reach the vehicle. It may be feasible to charge up condensers on the satellite and propel the negative plates out into space until a coulomb or so of negative charge has been disposed of. For example, balloons with metallized surfaces could be pushed out a porthole, inflated, charged up, and propelled into space. Each would carry off a certain amount of charge. Another approach would be to use a hot filament to inject electrons into the earth's magnetic field where they would be trapped and prevented from returning to the vehicle.

Unconventional Shielding of Electrons

Trapped electrons appear to pose no great problems to personnel or materials that can be protected by a reasonable amount of structure. Optical components and solid state devices such as solar cells may have to be located outside the structure for operational reasons and are not so readily shielded. For this reason, magnetic or electrostatic shielding may be worth considering. Magnetic shielding has the advantage of being effective for both electrons and protons, while electrostatic shielding could be used for unmanned vehicles in the outer Van Allen belt where protons would not be bothersome.

Effects of Natural Space Radiation on Materials

There is presently considerable data available on the effects of electrons on materials. A great deal of x-ray and gamma ray data is also applicable since secondary electrons are produced by the interaction of high energy photons with matter. In general, the electron's charge is responsible for its interactions with materials. Electrons lose energy by producing ionization and excitation of the orbital electrons of the constituent atoms and molecules. The observed radiation effects are then largely due to the subsequent behavior of the ionized and excited molecules.

Protons are singly charged also and produce ionization and excitation in a manner exactly analogous to electrons. * A priori, the ionization and excitation effects of a proton will be identical to the effects of an electron that deposits energy in the sample at the same rate, i.e., same linear energy transfer or stopping power or $\frac{dE}{dx}$. However, additional interactions occur with protons, particularly protons over a few hundred Mev.

Protons that stop in material, lead to interstitial hydrogen. The effects of this, using actual spectra have not been evaluated. Protons are also capable of nuclear interactions with cross sections measured in millibarns (14,15). These reactions are unlikely compared to ionization and excitation with cross sections equivalent to millions of barns. However, the ranges of high energy protons are so long that a sizeable fraction of the protons, perhaps as many as 1/10 or so, will undergo a nuclear reaction of some sort before being stopped. These reactions include meson production, spallation, and inelastic scattering.

* Incidentally, reporting proton dose in roentgens is a little questionable since roentgens can be stretched to apply to ionization, and protons lose as much or more energy by excitation than by ionization. Absorbed dose in rad or ergs/gram is much more applicable.

The importance of these reactions has not been assessed with respect to the proper behavior of materials in the high energy radiation environment of space. Additional basic cross section data on these reactions is very desirable, particularly in the high energy proton range.

Further radiation effects discussion will consist of sketching the problems of three arbitrary classes of materials:

- 1) usual engineering materials protected by a reasonable amount of structure
- 2) materials which are not normally shielded by structure
- 3) biological materials (man)

No serious problems appear in engineering materials protected by a reasonable amount of structure. Trapped electrons are completely shielded and the resulting bremsstrahlung are negligible. Such materials should be quite unaffected by proton doses of a few hundred rad from solar cosmic rays and proton dose rates of a few tens of rad per hour from trapped protons.

Solar cells, and optical components may have to be located on the outside of the vehicle structure to function properly. Our calculations show dose rates up to 10^8 rad/hr of unshielded electrons in the trapped radiation belts. There is some data on the effects of electron doses on solar cells (16). There appears to be significant damage at 10^7 rad of 300 Kev electrons so some provision must be made for shielding such devices. Glass plates have been used but radiation induces color centers in transparent materials cutting down their light transmission. Optical shielding is needed that does not lose its transparency. This might be accomplished by permitting the thin region affected to flake off exposing a new surface or by incorporating a provision for annealing out the color centers possibly by heat from the sun. It may be necessary to shield sensitive components by burying them in the structure of the vehicle and conducting light or infrared to them by front surface mirrors which would not be affected by the intense radiations in space.

Biological materials are the most sensitive materials which must be shielded from the natural radiations in space. Accordingly, shielding materials and configurations must be evaluated on the basis of how well they shield materials, and configurations must be evaluated on the basis of how well they shield people. The greatest uncertainty appears to be the biological effects of protons. At the high energy end of the spectrum, spallation and meson production in tissue must be evaluated. At the low energy end, the mechanisms of energy deposition do not appear to be too well known and should be better defined. All these effects are lumped into a parameter called the relative biological efficiency (RBE). The tissue dose in rads (due to ionization and excitation) must be multiplied by an RBE for the spectrum in order to get a number related to actual biological tolerances.

REFERENCES

1. Corliss, W. R., "Nuclear Power in Outer Space," *Nucleonics*, Aug 60.
2. Finger, H. B., "The Case for Nuclear Energy," *Nucleonics*, Apr 61.
3. Harvey, D. G., and Morse, J. G., "Radionuclide Power for Space Missions," *Nucleonics*, Apr 61.
4. Klein, L. T., "Interim Report on Safety Procedures for the Task 2 Thermoelectric Generator," MND-P-2335.
5. Klahr, C. N., "Scattering Shields for Space Power," *Nucleonics*, Apr 61.
6. Jacobs, G. J., Edited by, "Proceedings of Conference on Radiation Problems in Manned Space Flight," June 60, Washington, D. C. - NASA TN D-588.
7. Peters, B., Progress in Cosmic Ray Research Since 1947, *Jnl of Geophysics Research*, February 59.
8. Ney, E. P., Winckler, J. R., & Freier, P. S., Protons from the Sun on May 12, 1959, *Phys. Rev. Letters*, 15 Aug 59.
9. Sternheimer, R. M., Range-Energy Relations for Protons in Be, C, Al, Cu, Pb, Air, *Phys. Rev. Vol. 115 #1*, p. 137, 1 Jul 59.
10. Van Allen, J., Geomagnetically Trapped Corpuscular Radiation, *Jnl of Geophysics Research*, Nov 59.
11. Newell, H. E., & Naugle, J. E., "Radiation Environment in Space," *Science*, 18 Nov 60.
12. Freden, S. C., White, R. S., Particle Fluxes in the Inner Radiation Belt, *Journal of Geophysics Research*, May 60.
13. Hess, W. N., The Radiation Belt Produced by Neutrons Leaking out of the Atmosphere of the Earth, *Journal of Geophysical Research*, Oct 60.
14. Jarmie, N., & Seagrave, J. D., "Charged Particle Cross Sections," LA-2014.
15. Smith, Darryl B. (editor), "Charged Particle Cross Sections, Neon to Chromium," LA-2424.
16. "Nuclear Electronics Effects Program," Fourth Triannual Technical Note WADD TN 60-241.

TRANSPARENT MATERIALS

Chairman

Mr. W. Conrardy

Speaker

Mr. R. Wittman

Panel Members

Capt G. H. Roberts

Mr. K. H. Digges

TRANSPARENT MATERIALS

R. Wittman

Directorate of Materials and Processes, ASD

In any discussion of optical materials, the most important single parameter is wave length. A portion of the electro magnetic spectrum ranging from 0.150 to 20.0 microns is reviewed herein. The three definite areas included in this bracket are the ultraviolet, visible, and a portion of the infrared. In order to illustrate current capabilities and limitations, materials will be discussed under the type of application for which they are best suited.

Ultraviolet

Transmission of the ultraviolet wave lengths in windows and ophthalmic transparencies has been and is undesirable. Plastics used for this purpose have UV absorbers incorporated in the polymer structure to reduce transmission in the erythema (sunburn) band. Military specifications for plastic window materials require less than 5 percent transmission between 290 and 330 millimicrons. Ophthalmic transparencies are more restrictive in this respect and specify when possible, less than 1 percent transmission between 200 and 320 millimicrons. The transmission of soda lime glass, which is the composition most used in aircraft, does not exceed 5 percent up to 325 millimicrons. Ultraviolet radiation has no noticeable detrimental effect on glass but over a period of time does tend to degrade acrylic plastics. This effect however is not of such a magnitude as to warrant its consideration in crew enclosure design. The transmission curves for glasses having higher use temperatures than soda-lime do move further out into the ultraviolet as is shown in figure 1. Each application of these special glasses will present an individual problem which can be alleviated through the use of compensating coatings and/or filters, depending on the severity of anticipated conditions.

Visible Spectrum

Windows for vision in Air Force vehicles are constructed primarily of soda-lime glass and acrylic plastics. The most widely used single material today is the thermoplastic polymethylmethacrylate.

The evaluation of methylmethacrylate formulations toward the presently used modified acrylic (MIL-P-8184) is well known. Also the introduction of laminated acrylic sheeting with a polyvinyl butyral interlayer to provide a non-shattering glazing material.

The subsequent development of a practical method to induce molecular orientation in the thermoplastic acrylics through a hot stretching technique has fostered more efficient design of windows. Material thicknesses have been reduced and attachment means simplified. The "toughness" or resistance to fracture imparted by this process is determined by a special testing method which measures the amount of work necessary to propagate a fracture. Results are reported in terms of a "K" value which is equal to $1.25 (P/t) V_Z$ lbs/in.^{3/2}

Where:

t = thickness, in inches

B = width, in inches

P = ultimate load, in pounds

$Z = Y(2 - Y^2 - Y^4)^2$

$Y = X/B$ where X = width of fracture (in.) at point of instability.

The universal application of this development is shown by the fact that stretched acrylics have been incorporated into practically all operational USAF flight vehicles which require plastic windows. The polyester type thermosetting plastics cannot be oriented in this, or any other, fashion due to the high amount of cross-linking within the polymer. The operational use to date of this type of plastic has been quite restricted because of this limitation and the additional weight imposed by lamination.

In recent years, the Air Force has conducted several research programs aimed at the discovery and development of more thermally stable transparent plastics. Silicone materials have been studied extensively and formulations have been produced that have excellent thermal stability. But as yet it has not been possible to circumvent the inherent property of the silicone structure: that of resiliency and elasticity, consequently the strength properties of rigid sheet material even at room temperature are quite low. A more recent development sponsored by the Air Force has been the modification of a two-stage thermosetting acrylic plastic to produce a polymer that is structurally useable, from the standpoint of rigidity and strength, to temperatures of over 400°F. Attempts to achieve molecular orientation of this material while in the partially cured state were not too successful. It was possible to stretch the material mechanically and the optimum parameters were defined. However, the temperatures required to complete the curing of this material produced difficulty in maintaining the mechanical stretched stage. In the final product the orientation achieved was not of sufficient magnitude to warrant the use of this process. Figure 2 contains several properties of this developmental material.

Advancements have also been made by industry with the polyester family of materials and under other contracts within the Department of Defense on epoxy type materials which are quite transparent in the visible range of the electromagnetic spectrum. The capability of these modified materials insofar as strength retention at higher temperatures is concerned, is between 300 and 350°F.

The work on silicone polymers however has produced a material for use as an interlayer in laminates. The temperatures required to cure the interlayer are such that this material cannot be used effectively with plastics, and therefore has been utilized solely with glass. The need for an interlayer material having better temperature resistance than polyvinylbutyral and which would be compatible with plastics was recognized. Subsequently, such a material was developed and proven feasible by private industry. This "Cast-in-place" interlayer has made possible application of a composite concept which utilizes a non-structural outer ply of a more heat resistant notch sensitive plastic, the interlayer, and an inner structural ply of commercially available hot stretched acrylic. Aerodynamic generated temperatures beyond the normal capabilities of the structural member can be accommodated by a unit of this type. Research is continuing to define the best materials combination and to obtain criteria which will allow for the most effective design parameters with this composite concept.

Two standard interlayer materials are currently available for use in glass laminates. Polyvinylbutyral has been used for many years as a flexible sheet material to impart

shatter resistance to both glass and plastics. It is quite easy to use in fabrication, and has been generally suitable in most respects although certain design considerations have had to be made to compensate for its elevated temperature stability (under 200°F) and low temperature resiliency. Previous mention was made of the development of a silicone type interlayer material which can be used at temperatures up to 300°F and still retains its elastic properties at very low temperatures. An improved silicone material having a temperature capability of approximately 425°F is under evaluation at the present time. Figure 3 gives a comparison of interlayer materials for the function of impact resistance versus temperature when laminated with glass and shows the obvious advantages of the silicones.

The glass composition used for aircraft windows today is that of soda-lime or commercial plate glass. This glass has satisfied materials requirements for visual capabilities, strength, temperature resistance, and in the laminated form, impact resistance. Other compositions having much higher temperature capabilities have been developed by the glass industry over the past few years. These glasses and their approximate capabilities temperaturewise are shown in figure 4. Actually at the time of development there was no need for these glasses, at least not for use in crew enclosures. However, specific requirements today have made the application of these glass types mandatory. It is definitely a big step to produce these glasses in sizes and of the quality necessary for aircraft windows. Two very important factors are: quality from a materials as well as an optical standpoint. It is relatively simple to obtain quality soda-lime glass for flight vehicles by the simple selection of the highest quality glass from a large volume of plate glass produced for industrial purposes. However, only a small portion of commercial production meets the rigid Air Force optical requirements. Rejected glass is diverted into the normal production cycle. The more heat-resistant glasses are not produced in as large a volume, therefore, the Air Force has sponsored a program over the past three years to develop a feasible manufacturing method to insure the production of a consistently acceptable heat resistant glass. This program has been carried out quite effectively and production methods have proved practical. The program has also evolved several improvements in glass finishing techniques, all of which are designed to increase the reliability of glass components. In addition, the Air Force has and is sponsoring a program at the National Bureau of Standards to obtain useable design criteria on these glasses at temperatures up through the capability of each particular glass involved.

Research and development efforts on ophthalmic transparencies have incorporated and put into practice much of the knowledge gained on window materials, such as hot-stretched acrylics, laminated polyester plastics, and conductive coatings for de-misting purposes. Research towards modifications of present plastics is being conducted to produce ophthalmic transparencies having higher transmission in the visible range and greater reflectivity in the infrared. Ideal condition and available materials are shown in figure 5. Other programs are directed toward self attenuating ophthalmic filter materials to provide eye protection from nuclear flashes. Phototropic compounds are being investigated for this application.

The availability of higher temperature glasses that have the necessary quality for more advanced Air Force applications, together with publishing of mechanical design criteria, is a large step forward. To utilize these glasses at temperatures where conventional direct attaching techniques are impossible, the Air Force has over the past four years sponsored research on attachment materials and techniques. This work has resulted in successful direct bonded attachments for soda-lime glass good for extended lengths of time at 500°F. In addition to the temperature capability of the attachments their use has made it increasingly possible to use windows as structural elements. Further developments

have produced attachments compatible with lower expansion high temperature glasses and having a load carrying capability to 900°F. This program will continue to increase the operating temperature range and to provide design criteria from which to produce practical high temperature glazing assemblies. The most recent effort in the area of attachments is to produce a bonded attachment primarily for alumina windows which have a temperature capability of 2500°F for at least five minutes.

Within the area of visible light transmission some mention should be made of coatings which are used for de-fogging and de-icing purposes on windows and ophthalmic transparencies. Most aircraft today have glass incorporating these coatings primarily in front and side windows. The coatings are effective and tribute is certainly due to the suppliers for their research and rapid advancement of techniques in this area. The bulk of window replacements in today's flight vehicles, are due to the failure of this coating, rather than the glass itself. Close cooperation between the airframe manufacturers and window suppliers in the design stage is very critical. Concepts are being altered and revised to provide the necessary considerations generated by characteristics of coatings and their preservation under the severe aerodynamic and structural performance requirements of today's air vehicles.

As we make our initial explorations into space travel, the use of transparent materials in vehicle design is mandatory. Data on the capabilities of presently available transparent materials under all natural and predicted environments are not complete. The known basic materials properties make transparent glasses and plastics appear marginally satisfactory providing proper design considerations are used.

The exposure time to known natural and induced environments of transparent materials installations, with the exceptions of high vacuum, radiation, and micro meteoritic particle impact, will generally be a few minutes during initial powered flight, and again during a re-entry and landing phase. The areas of greatest concern are those of possible explosive decompression due to materials or structural failure, temperature effects, and loss of a clear vision area during flight.

To provide more reliable design criteria, additional research studies are being made at elevated temperatures on the spectral emissivity and heat transfer capabilities of coated glasses, combinations of transparent materials and coatings, and changes that occur when abraded surfaces are introduced. Data in this area is valuable not only from the material aspects but also the secondary effect on the internal conditioning system of the vehicle.

Controlled abrasion of glass does not materially reduce design strengths but the effects of random micrometeoritic and charged particle impact on the erosion characteristics under high vacuum and extreme temperature conditions must be learned.

Areas that are generally related to individual vehicle design such as vibration effects and methods of mounting (seals), can and are being investigated on a laboratory scale, to define and provide materials requirements and effective design data under high vacuum, and re-entry temperatures. Initial structure designs will then be more tailored to the materials restrictions, if any, imposed by mounting requirements.

To obtain statistically reliable design data on known special glass compositions under high stresses at high temperatures over long periods of time, will continue to be necessary together with related basic properties data. The continuous upgrading of the state of the art in the production, processing controls, and fabrication techniques by industry, coupled

with integration of these improvements into window design will further increase the efficiency and reliability of our present optically transparent materials.

Infrared

Transmission in the wave length band from 0.7 to 20 microns is by far the broadest of the groups within the scope of this review. The most important parameter for consideration is infrared transmission, but the practical and even experimental use of a material is dependent upon the perfection of its processing, to insure homogeneity, and optical uniformity.

One of the most important requirements right now is that of retention of transmission efficiency together with mechanical integrity at elevated temperatures. Desirable properties toward this end include low thermal expansion and light weight. Most materials either being used now or being considered for use in this area are of a brittle nature. Fracture and/or failure of an item is generally due to the presence of flaws within the material. Again the importance of consistent quality is evident.

A new or better material which appears to have the desired properties such as transmission, quality, and temperature stability, cannot be utilized unless it can be produced in the proper form. This is a recognized problem whose importance is as great as the research and discovery of new materials.

Window materials which have been used in airborne infrared systems include optical glasses, fused silica or quartz glass, calcium aluminate glasses, arsenic sulfide glass, silicon, Kel-F and silver chloride. The effective transmission limitations for these materials range from 2 microns out as far as 6 microns under ideal conditions.

The Air Force has sponsored studies on other materials including intermetallic semiconductor compounds, refractory oxide and sulphide glasses, antimonate glasses and sintered barium-fluoride. Industry has, both through company sponsored research and as contractors and sub-contractors through the Department of Defense carried out a considerable effort in this area. Comprehensive data and bibliographies on all infrared transmitting materials has been compiled and released by several organizations under contract to the Government. There are also in effect today many research studies designed to provide design criteria on infrared transmitting materials when subjected to hyper thermal and extra terrestrial environments.

Advancements with and improvements of available infrared materials are continuing. One such development is the work by the Barr and Stroud Company, Glasgow, Scotland on calcium aluminate glass to remove the absorption band between 2.5 and 5 microns. Figure 6 shows a comparison of the Barr and Stroud modification and a typical calcium aluminate glass. Other notable developments by industry include Eastman Irtran I and II, Eastman Kodak Co., Rochester 4, N. Y. Irtran I appears good for shorter wave lengths (less than 5 microns) and at temperatures up to approximately 800-900°F. Irtran II has good transmission in the band of 8 to 13 microns but more knowledge of these materials and their limitations, especially in sections thick enough for use as external windows together with their mechanical behavior at elevated temperatures is needed. Figures 7 and 8 are the transmission curves on these materials at temperatures up to approximately 1470°F.

The necessity for producing infrared transmitting windows in useable shapes prompted an Air Force contract which has just recently been completed by The Texas Instrument

Company. The material selected for this program was silicon. The production of cast domes up to 8 and one-half inches in diameter was made feasible through this effort. Transmission of silicon out to 8 microns is good, however, as higher temperatures are imposed, the transmission is reduced and at approximately 900°F becomes essentially zero. The availability of large windows of silicon will make possible more widespread application of this material within its useable temperature and transmission ranges.

Currently, ASD has a contract concerned with the development of high energy pressing techniques to produce IR Domes of desirable shapes and sizes. Materials being investigated include barium and calcium fluorides, cadmium and magnesium oxides, and calcium oxide.

A considerable portion of the materials research and development in this area is conducted in support of specific equipment contracts for solution of particular problems. One fundamental materials study recently initiated directly by the Air Force however is concerned with Gallium Arsenide. This material appears to have good transmission characteristics from 2 to 20 microns and relatively good temperature resistance.

Research on materials for ophthalmic transparencies is directed toward the absorption of infrared wave lengths. Present requirements are for maximum transmittance of 1 percent between 800 and 2000 millimicrons. This requirement becomes obvious when it is considered that approximately 40 percent of the thermal energy from a nuclear flash is in the infrared region. At the same time infrared reflection is necessary, transmission in the visible range is not to be reduced.

Other infrared optical components have not normally been considered in the materials research and development programs. This would include such items as mirrors, selective filters and detector cell windows.

Re-Entry Air Vehicle Window Concept

The human eye's ability of retentivity of vision permits one to have good vision through a disc containing holes or slots when it is rotating at sufficiently fast rate. One can readily understand this after realizing it is the same effect as that of seeing through the rotating blades of a fan or aircraft engine propeller.

Based upon this principle, a concept was developed by two ASD engineers: how one could have vision during re-entry heating periods and also maintain relatively modest temperatures on a transparent material located behind a rotating slotted disc. The latter feature is achieved because of the following facts. The rotating disc could be made of an insulating material with a high surface emissivity. To augment the heat impedance of the disc, a cooling gas could be injected between the rotating disc and the window. At any instant only a small ever changing portion of the window is exposed directly to the heat coming through the slots in the disc. Figures 9 and 10 show views of the original model based upon this concept.

To demonstrate feasibility of the idea several questions required answering: Could one see adequately through a rotating slotted disc at high temperatures? Would the requirements for cooling be reasonable? To answer these questions light transmission, heating, and simulated re-entry tests were undertaken.

Light transmission values obtained from the rotating disc were equal to the percent of open area cut into the disc. The minimum light transmission requirement for landing a

vehicle at dusk is approximately 12 percent, and for a moon lit night 16 percent. Hence, all disc configurations having more than this percent open area were more than adequate. Still photographs and motion pictures were taken under ambient and high temperature conditions. Excellent photos were obtained regardless of the number of slots in the disc and motion picture quality was controllable by adjustment of rotating speeds versus shutter speed. Results of tests in a high temperature, hypersonic gasdynamic facility are shown in figure 11.

The surface temperature of the rotating disc was above 2200°F while the maximum temperature on the outside glass surface was 780°F and the inside surface remained below 400°F. Air temperature was above 3100°F.

This concept has been shown to be practical. What is needed is further designing and testing to develop a window for specific hardware applications. Although the original application conceived for this device was human vision, several others are possible. Proper modifications may remove the need for the glass member and permit full transmission of the electromagnetic spectrum. This is only speculated but is a potential.

Summary

Transparent materials window requirements for the areas previously discussed are both specific and of a general nature.

- a. Ultraviolet transmission is discouraged while simultaneously improving response in other portions of the electromagnetic spectrum.
- b. Plastic, visible light transmitting, materials are needed which have a temperature capability to over 800°F for use as rigid members and for interlayer applications. Also for rigid, optical quality plastics which transmit neither above or below the visible spectrum.
- c. More efficient processing of glassy materials to satisfy requirements such as increased reliability and more effective design.
- d. Additional data on the behavior and properties of window materials when subjected to predicted space environments.
- e. Development of infrared transmitting windows having high transmission through 15-20 microns and at temperatures up to 1500°F.

In this age of rapid scientific advancement, our continuing research studies will certainly produce materials which will surpass these generalized requirements. It is really a matter of first things first, by meeting each immediate challenge with the right answer in the shortest time.

Bibliography

1. Specification MIL-P-8184 Plastic Sheet, Acrylic Modified
2. Optical Requirements for Ophthalmic Transparencies - WADD Unpublished
3. Materials Handbook Corning Glass Work 1958
4. Batzdorff, A., Gouza, J. J., Hurst, D. A. - The Investigation of Multiaxially Stretched Acrylic Plastic WADC TR 54-619 Parts I and II 1957
5. Transparent Glazing Materials for Flight Vehicles - MIL-HDBK-Part II 1961
6. Helvey, G., Clark, H. A. Development of a Rigid Transparent Plastic Material Suitable for Aircraft Glazing at Elevated Temperature, WADC TR 56-352 Parts I and II 1958
7. Parker, E. E., St. Pierre, T. L., Stickley, W. E., George, E. A., Dzugan, M. R., Improved High Temperature Resistant Transparent Plastic Materials, WADD TR 60-72 May 1960
8. Development and Evaluation of High Temperature Resistant Composite Plastic Plates-Midwest Research Institute February 1961 (Bureau of Naval Weapons Contract No. as60-6099-c)
9. Evaluation of High-Temperature Cast-in-Place Transparent Plastic Laminates Suitable for Canopies on Supersonic Fighter Aircraft - Goodyear Aircraft Corporation - Bureau of Naval Weapons Contract No. a(s)59-6146-C Prog Rpts 1-6
10. Polmanteer, K. E., Campbell, F. J., Laur, T. L., Silicone Interlayer Material Program WADC TR 56-159 July 1956
11. Polmanteer, K. E., Campbell, F. J., Laur, T. L., Silicone Interlayer Material Program WADC TR 57-213 Parts I and II 1958
12. High Temperature Aircraft Windshield Development AF Contract 33(600)36852 Quarterly Progress Reports 1-10
13. Kerper, M. J., Diller, C. C., Eimer, E. H., Properties of Glasses at Elevated Temperatures, WADC TR 56-645, Parts II, III, IV and V.
14. A Summary of the Narmco, High Temperature, Glazing Edge Attachment Effort - Telecomputing Corporation 1961
15. Wittman, R. E. Optically Transparent Materials for Space Flight Vehicles WADD TR 60-203 April 1960
16. Materials Research, Development and Application Technical Symposium WADC TR 58-655 July 1958
17. Evaluation of BS-37A Glass - WADD - WCLRWI Internal Report 40513 - Parts I and II 1959

Bibliography (Cont'd)

18. Cole, R. L., Mitchell, G., Hicks, J., Development of Silicon Infrared Optical Components AMC TR60-7-719 December 1960
19. Elevated Temperature Studies of Infrared Transparent Materials - Contract N123-(60530)-2167A, Quarterly Progress Reports No. 4, November 1960
20. Ballard, S. S., McCarthy, K. A., Wolfe, W. L., Optical Materials for Infrared Instrumentation - IRIA Report 2389 - 11-S, January 1959
21. Allinkov, S., Forbes, F., A New Concept for Re-Entry Vehicle Windows - Presented at the ARS Structures, Materials and Design Conference April 1961

OPTICALLY TRANSPARENT MATERIALS

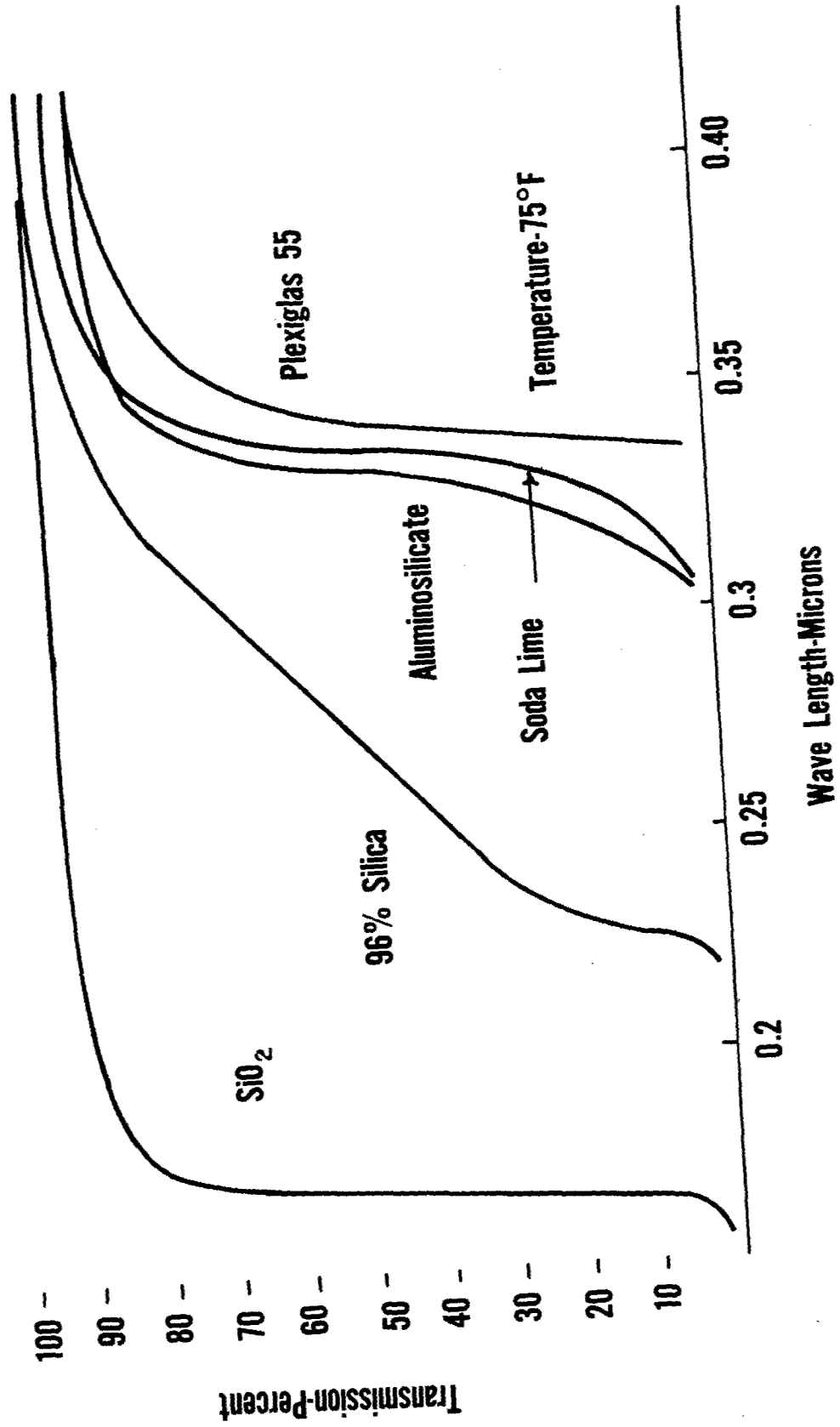


Figure 1. Ultraviolet Transmission

OPTICALLY TRANSPARENT PLASTICS

MODIFIED SELECTRON 400* (Formulation 796-55-4)

TEST METHOD

Flexural Strength @ 77°F psi 13,600	ASTM D-790-58T
Flexural Modulus @ 77°F psi 521,000	ASTM-D790-58T•
Flexural Strength @ 480°F psi 3,500	ASTM-D790-58T
Flexural Modulus @ 480°F psi 188,000	ASTM-D790-58T
Tensile Strength @ 77°F psi 6000	ASTM-D-638-58T
Tensile Modulus @ 77°F psi 503,000	ASTM D 638
Heat Distortion Temperature °F 516	ASTM-D648
Luminous Transmittance % 88.6	ASTM-D1003-52 Proc B
Haze % 1.5	ASTM-D1003-52 Proc B

*Pittsburgh Plate Glass Co.

Figure 2. Selected Properties of Modified Selection 400

INTERLAYER MATERIALS

IMPACT RESISTANCE VS TEMPERATURE*

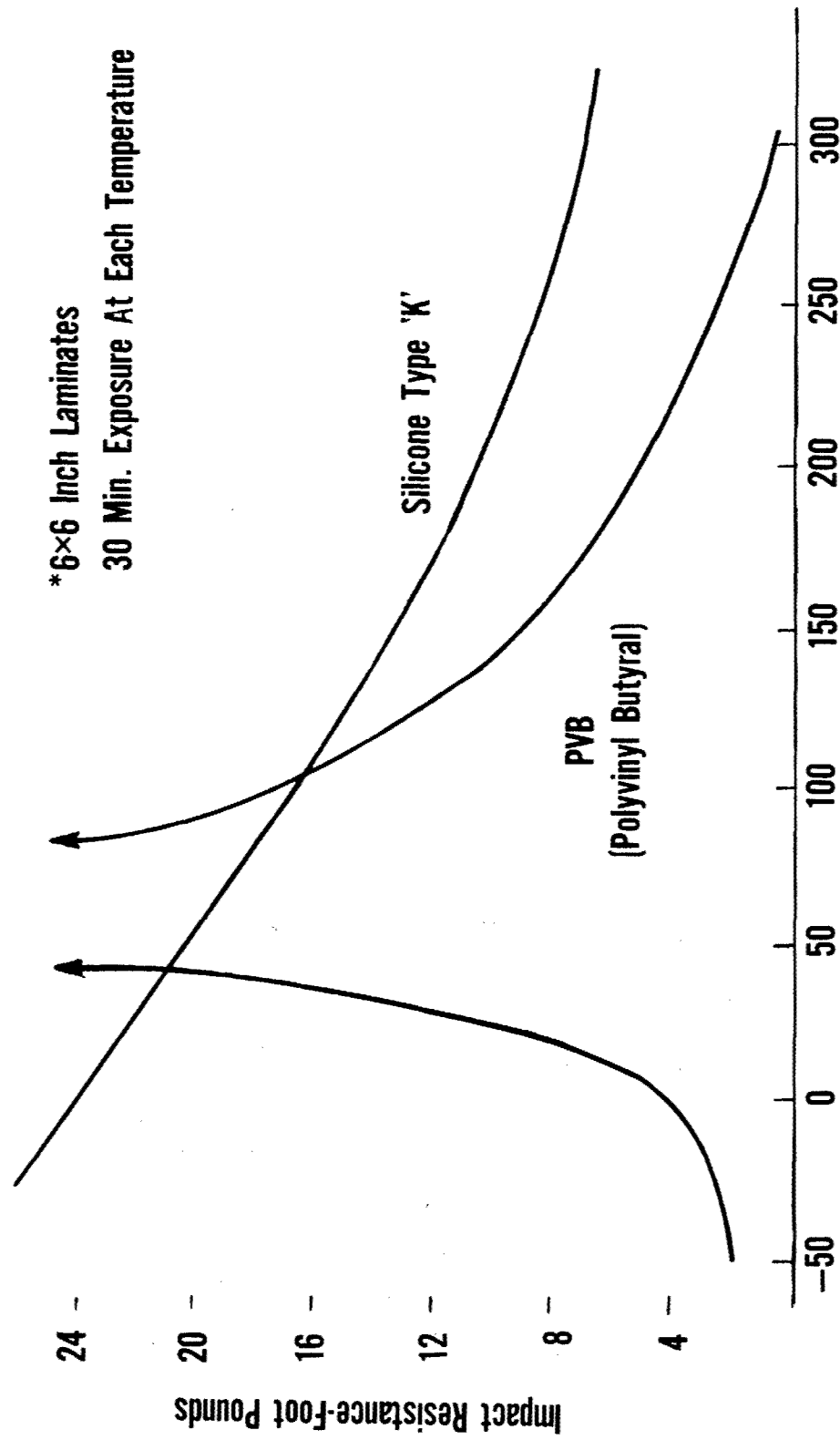


Figure 3. Relative Impact Resistance of the Interlayer Materials

OPTICALLY TRANSPARENT GLASSES

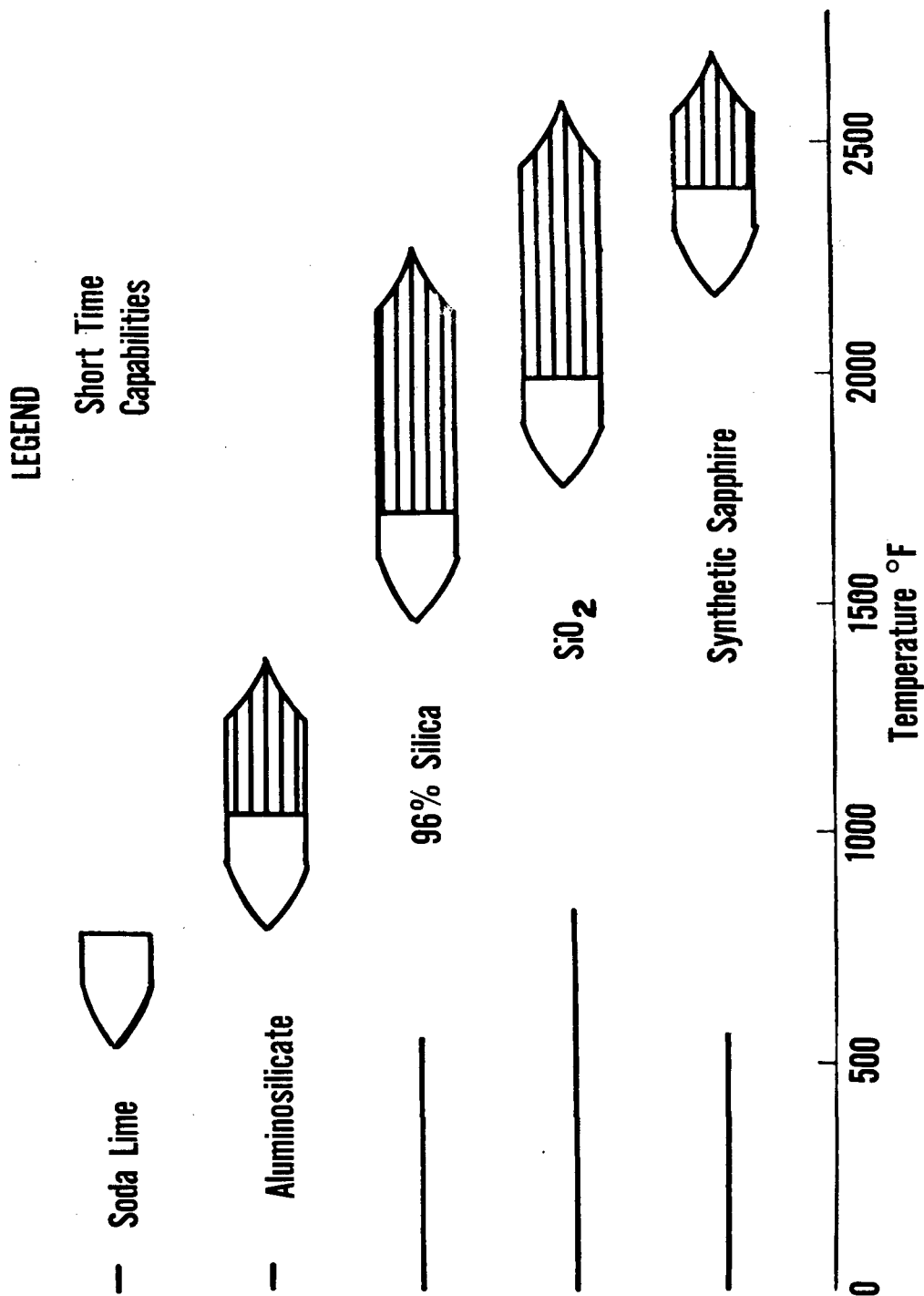


Figure 4. Optically Transparent Glasses

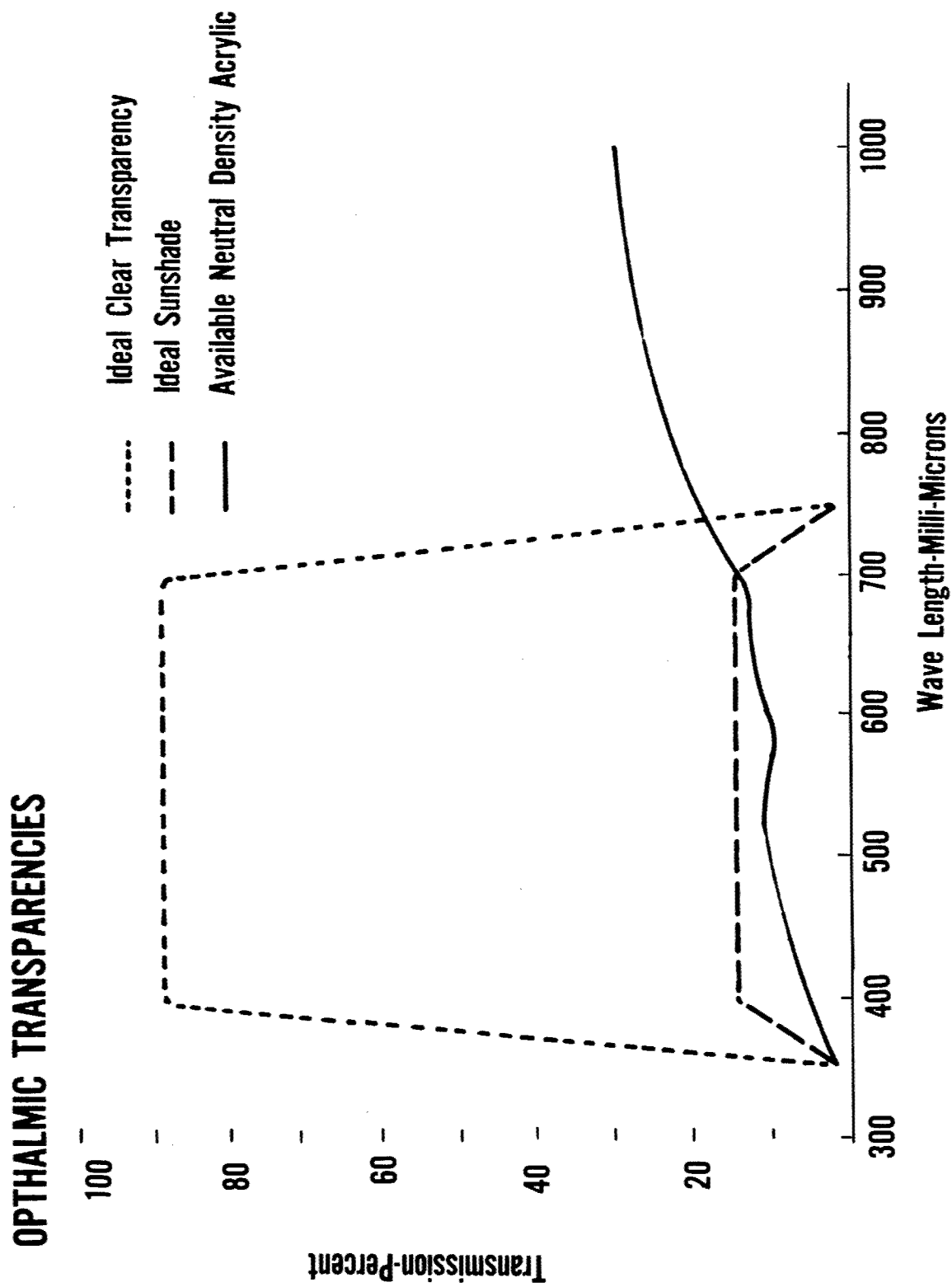


Figure 5. Ophthalmic Transparencies

CALCIUM ALUMINATE GLASS

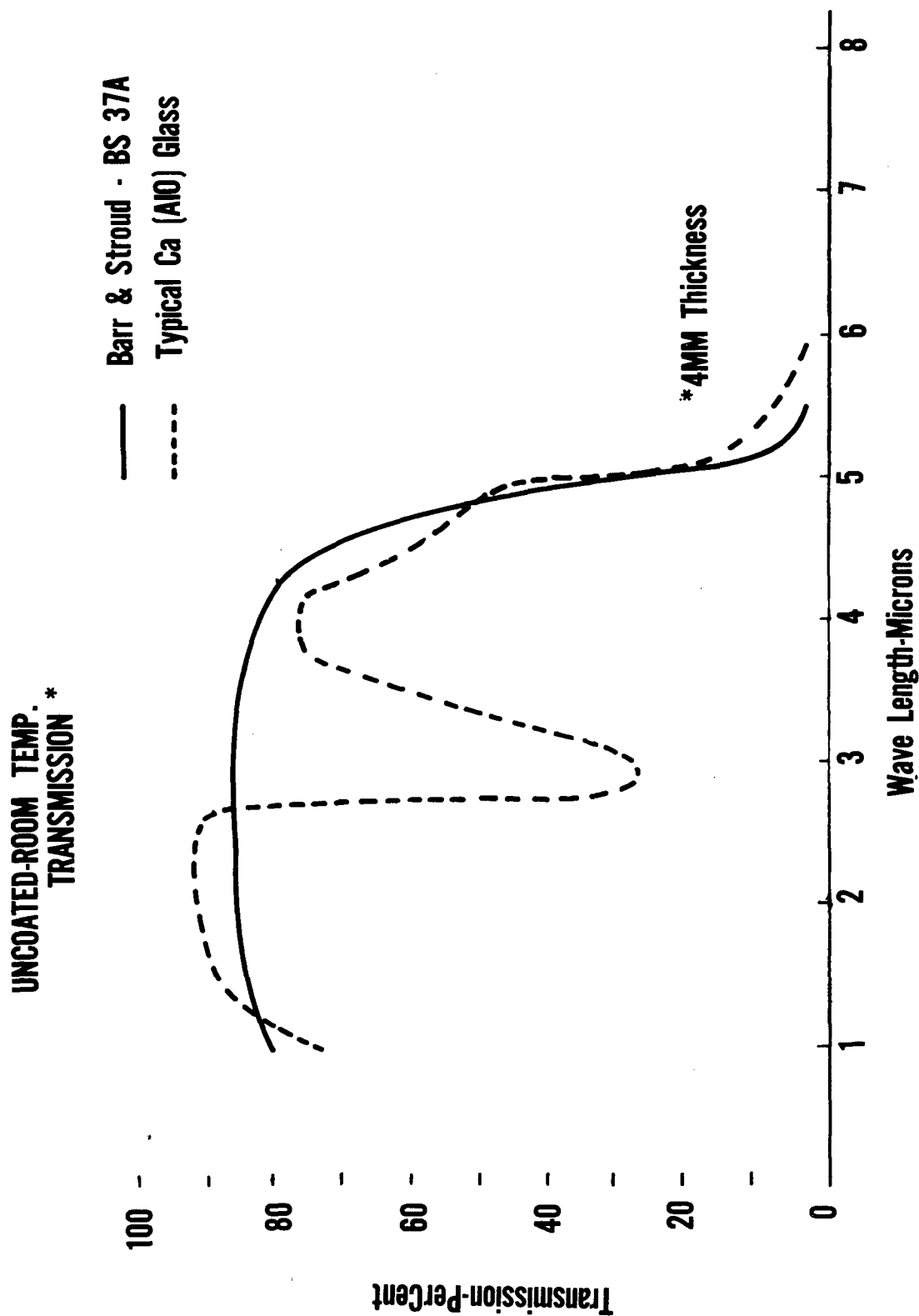


Figure 6. Transmission of Calcium Aluminate Glass

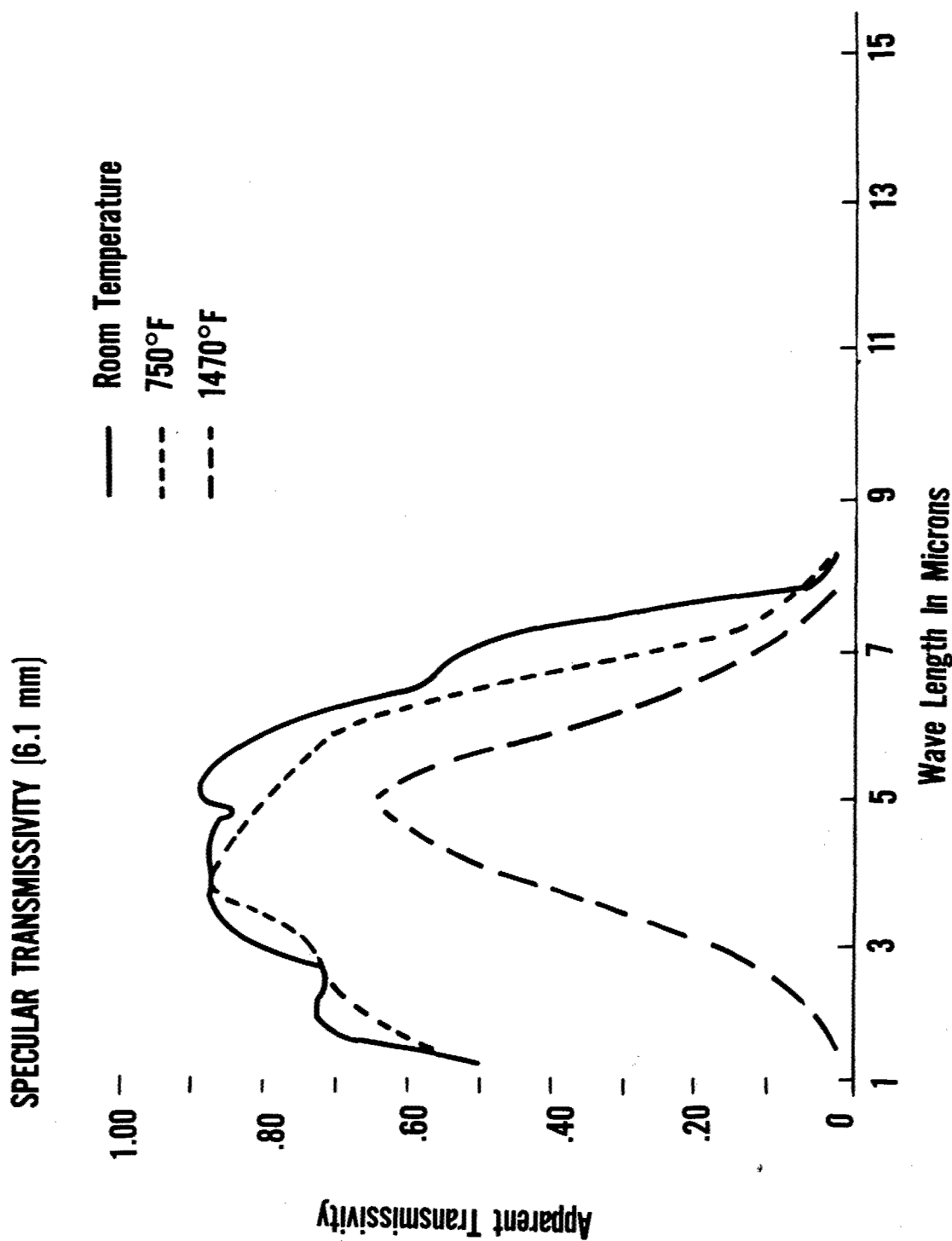


Figure 7. Infrared Transmission Versus Temperature

IRTRAN ABC-2 Std.

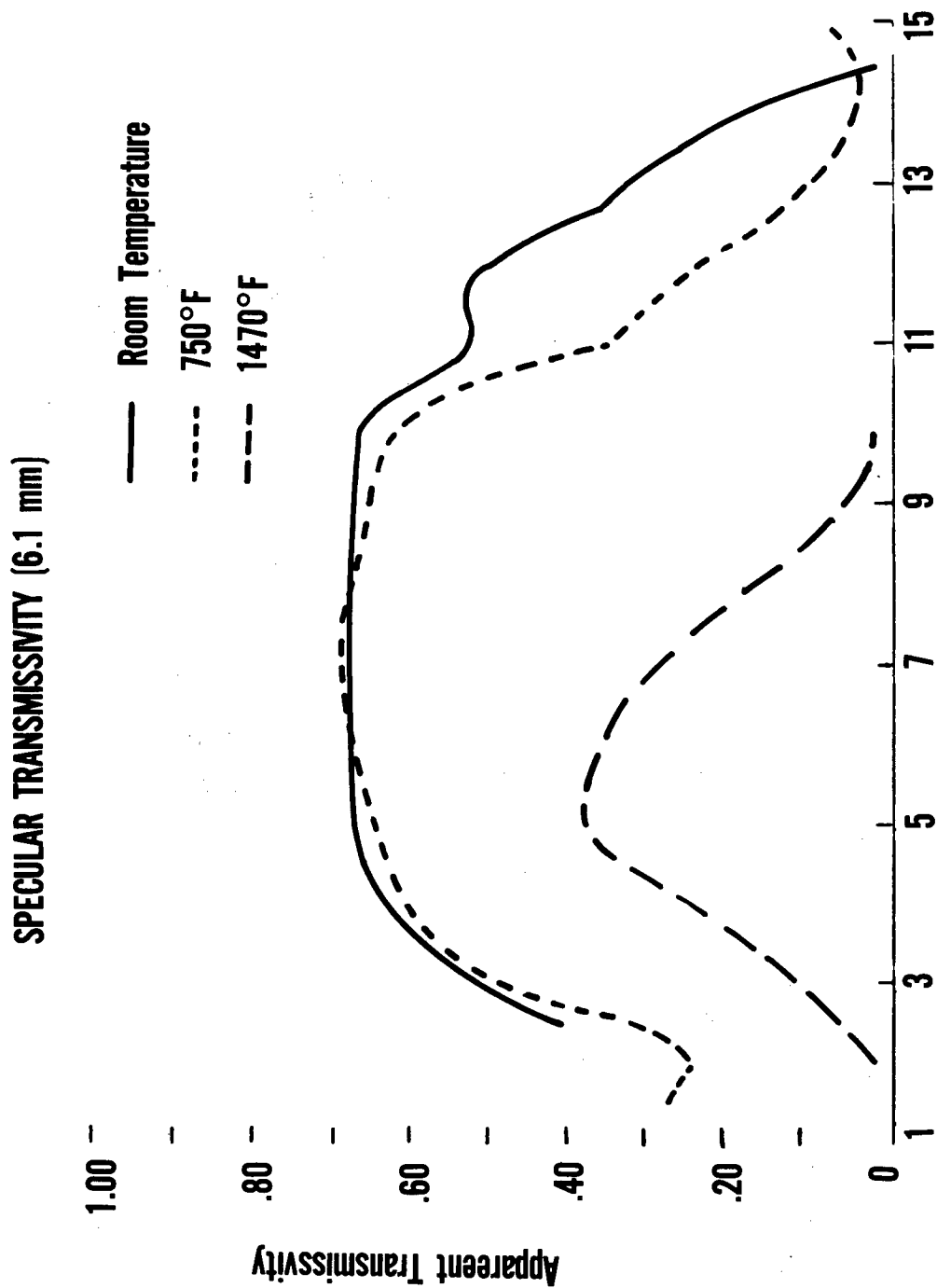


Figure 8. Infrared Transmission Versus Temperature

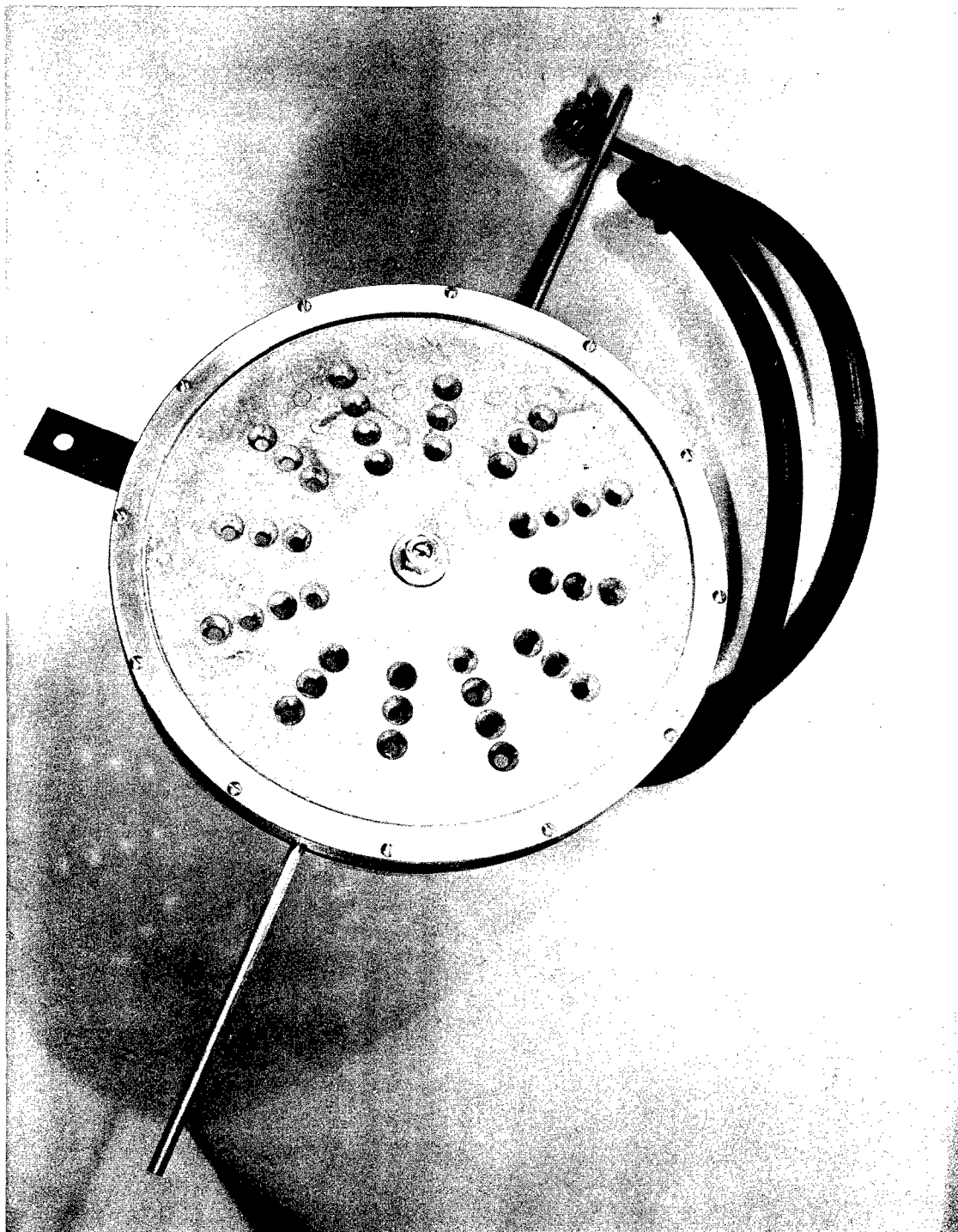


Figure 9. Front View of Original Re-Entry Window

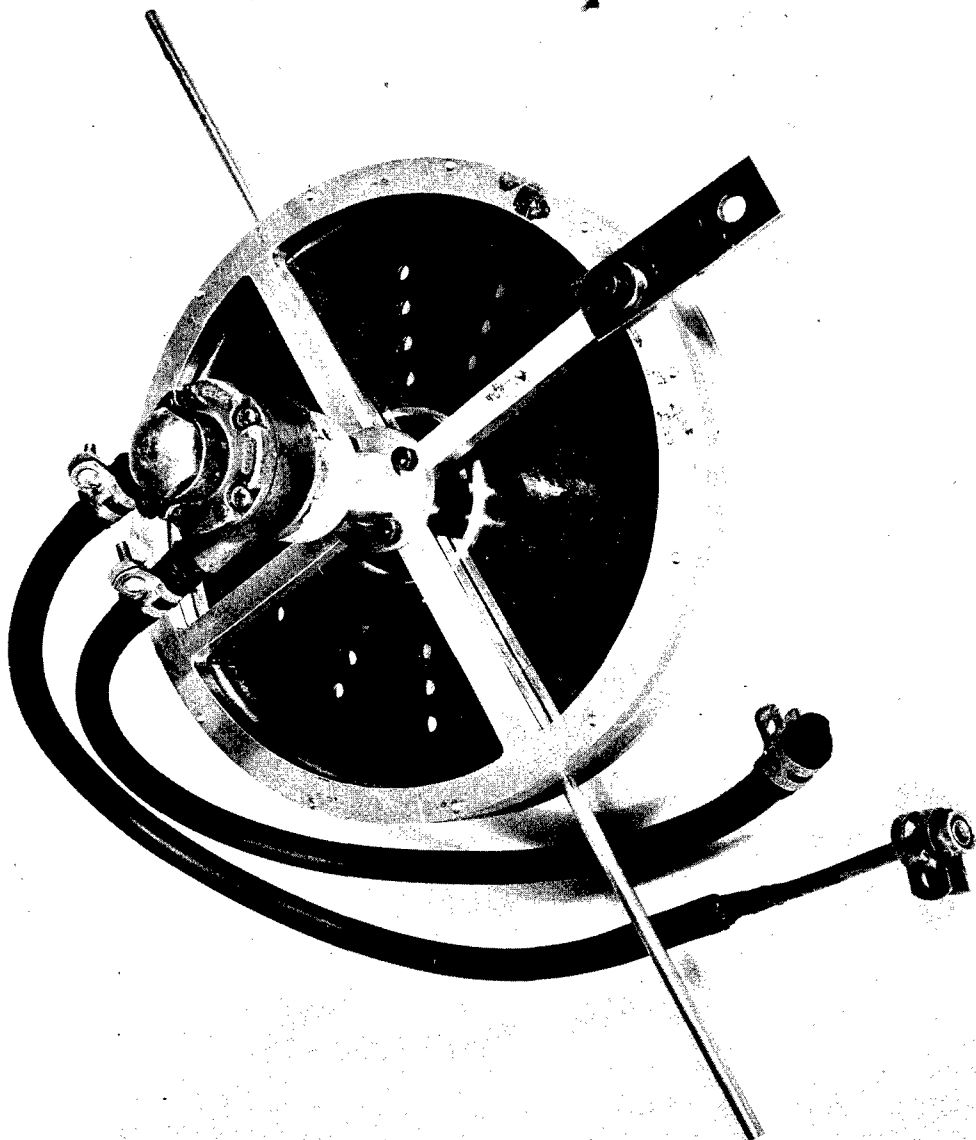


Figure 10. Rear View of Original Re-Entry Window

RE-ENTRY WINDOW

SIMULATED RE-ENTRY TEST DATA

LEGEND

Disc Configuration One Slot

Percent Open Area 2/3%

Revolutions Per Minute

Coolant-Helium-Flow, 0.3lb. Per Min.

Angle Of Attack-20°

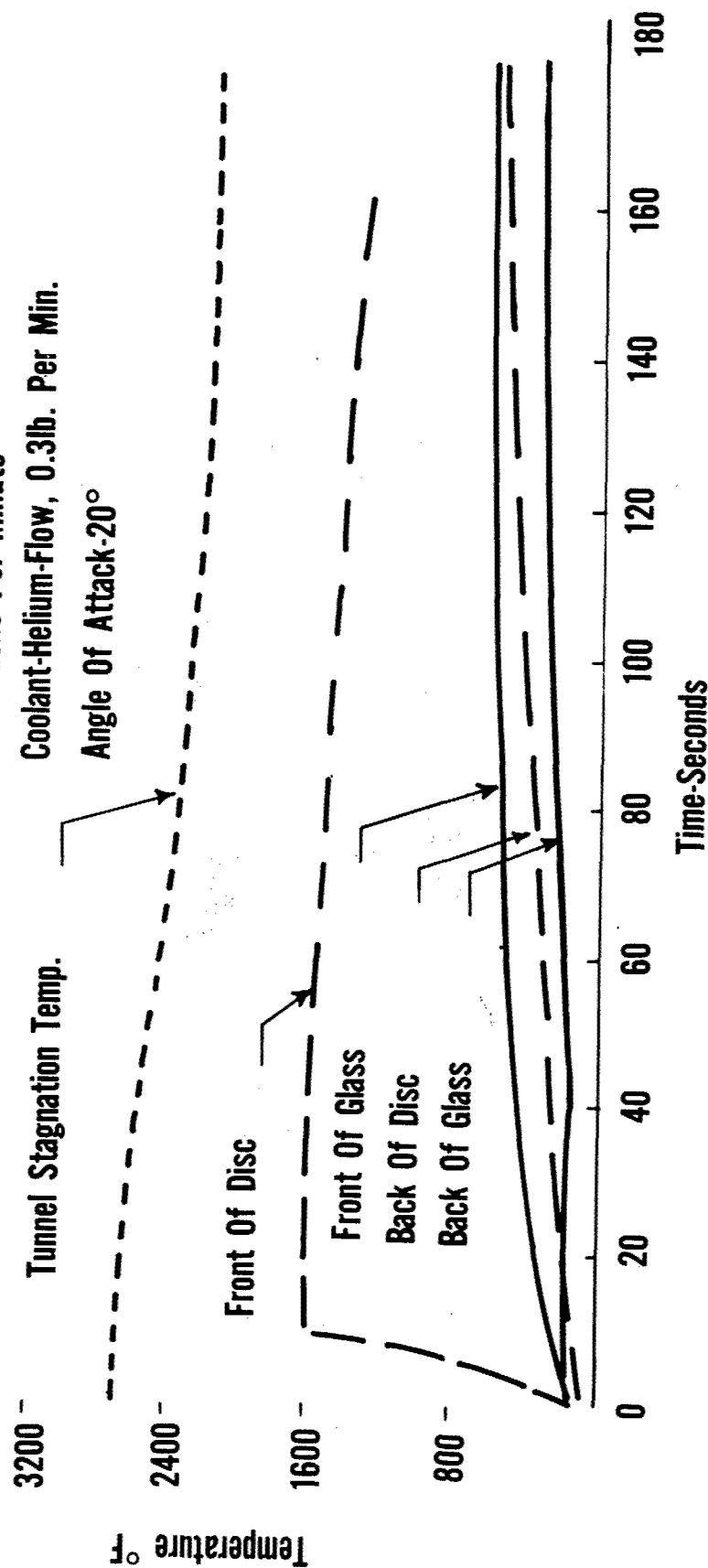


Figure 11. Temperature Distribution Through Re-Entry Window

UNIQUE METALLURGICAL RESEARCH STUDIES

Chairman

Mr. I. Perlmutter

Speaker

Lt. Col. E. M. Kennedy

Panel Members

Mr. W. G. Field (AFCRL)

Dr. H. Rosenberg

Mr. D. Langer

Mr. P. L. Hendricks

UNIQUE METALLIC MATERIALS AND TECHNIQUES

Lt. Col. E. M. Kennedy, Jr.

1/Lt. S. A. Worcester, Jr.

Directorate of Materials and Processes, ASD

The aerospace age has ushered in some of the most advanced developments ever to come from human imagination and ingenuity. Each new development has created problems which have severely challenged human engineering capabilities. Every branch of the engineering profession has been presented with problems of varying degrees of difficulty, each problem requiring a solution which substantially contributes to technological development. One of the most important areas today is materials engineering and development.

In the present Air Force metallic materials development programs, we find ourselves confronted with two major barriers—the temperature barrier and the weight barrier. In this first area, we must cope with the problem of developing materials with adequate strength and corrosion resistance for use at temperatures far in excess of 1800°F. The general approach to this problem has been to turn to the refractory metals, such as tungsten, tantalum, molybdenum, and columbium, for use as base materials, and then to rely on alloying or thermo-mechanical processing for increased strength, with simultaneously developed coatings to provide the necessary resistance to oxidation and/or corrosion.

The weight barrier has created the necessity of producing the maximum strength in a structure with a minimum of weight. Aside from the design criteria, we are faced with either making vast improvements in existing alloy systems or developing newer and better alloys. In examining new alloy systems, the Metals and Ceramics Laboratory has investigated the potentials of such metal systems as beryllium, scandium, yttrium, and the rare earth metals. Beryllium has emerged as the most promising of the newer metals investigated. Beryllium has a density comparable to magnesium with a melting temperature twice that of magnesium. However, certain problems, such as the lack of suitable ductility, have detracted greatly from these more desirable properties. In spite of the initial attractiveness of beryllium, we are far from having a suitable alloy which can be readily adapted to modern technology. Therefore, the metallurgist is busily engaged trying to develop some suitable light weight alloy system.

The development of new alloy systems is by nature a slow process; gains tend to be marginal and ultimately the approach is limited by the number of elements in the periodic chart. Realizing the marginal nature of the gain to be realized by sticking with standard or conventional techniques, the Metals and Ceramics Laboratory has initiated programs to investigate unique processes which might result in great strides forward in materials technology. Our efforts in many of these programs in the category of low probability-high payoff. It is this type program that we intend to cover in this presentation.

First, let us examine the state of the art in the field of the rare earth metals as we view them from the standpoint of being unique systems.

The term rare earths has been applied to the series of elements beginning with lanthanum, atomic number 57, and ending with lutecium, atomic number 71. Scandium

($Z = 21$) and yttrium ($Z = 39$) behave very similarly to the rare earths chemically and are, therefore, often included in considerations of the rare earth elements. These elements are often sub-divided into two groups--the "light" rare earths, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, and europium ($Z = 57-63$); and the "heavy" rare earths, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium ($Z = 64-71$). Scandium and yttrium are also generally included in the "heavy" rare earth group. The term "misch metal" refers to the alloy of the rare earths in the proportion in which they occur in the ore from which they are extracted. "Didymium" refers to an alloy of the "light" rare earths from which the cerium has been removed.

Rare earths have been used for some time as minor additions to engineering alloys. In various steels, rare earth additions increase melt fluidity, decrease tendency toward hot shortness, improve corrosion resistance, and improve impact properties. Cerium and misch metal can be used to produce nodular iron, with or without magnesium additions. Generally, rare earth additions to magnesium alloys impart better elevated temperature properties. Cerium additions are sometimes used in aluminum alloys for use in pistons for internal combustion engines. Small amounts of cerium increase the service life of nichrome resistance elements. In summary, additions of rare earths, such as cerium, lanthanum, or misch metal, are known to improve certain metallurgical properties of alloys. However, many reports are conflicting, and the question often arises, what are the metallurgical characteristics of the individual rare earths? Since individual rare earth metals have recently become available in sufficient quantity for metallurgical evaluation, a program has been undertaken to determine the mechanical properties, oxidation resistance, alloying characteristics, and other important metallurgical properties of the individual rare earth metals. The mechanical properties and oxidation resistance of the individual rare earth metals thus determined are shown in figures 1 and 2, respectively.

There is a considerable difference in the properties of the individual rare earths, but none of the rare earths have sufficient strength or oxidation resistance to warrant further intensive research effort on rare earth rich systems for structural purposes. Phase relationships have been determined and all available phase diagrams have recently been compiled by Love. There are many areas in which the rare earths warrant future effort, including the electrical, magnetic, and nuclear fields, but current Air Force interest in the rare earths in structural alloys is limited to their use as minor additions, particularly to the refractory metals. Two effects of minor additions of the rare earths are of immediate interest in refractory metal alloys: their effect on oxidation resistance; and, their effectiveness as scavenging elements and grain refiners.

Interest in the first effect stems from known effects of rare earth additions in improving the high temperature oxidation resistance of iron, nickel, and chromium-base alloys. Since columbium-base alloys have been developed which have a somewhat adherent and protective scale at elevated temperatures, the effect of rare earth additions upon these alloys and upon modifications of these alloys is being evaluated. The ultimate goal of this work is to develop columbium-base alloys which have adequate oxidation resistance with acceptable engineering strength and ductility.

Use of the rare earth metals as scavengers depends upon the strong affinity of the rare earths for oxygen. The addition of too much rare earth to a given refractory alloy results in rapid deterioration of strength and oxidation resistance. This deterioration stems from the extremely low solubility of the rare earths in the refractory metals, any excess rare earth being present has a deleterious second phase. Therefore, a program is cur-

rently being sponsored for the determination of the solubility limits of yttrium and scandium in chromium, molybdenum, tungsten, columbium, and tantalum.

Following this brief discussion of current interest in the metallurgical properties of the rare earth metals, it seems appropriate to discuss three unique techniques which are being explored by the Air Force in the search for advancement in materials technology. The first of these techniques, which warrants considerable discussion, is the application of high static pressure to materials. It should be emphasized that studies of this nature not only may contribute to materials technology through the production of new materials by the application of high pressure, but may significantly advance our understanding of important phenomena which occur at atmospheric pressure.

Since the synthesis of diamond and "borazon" (cubic boron nitride) by the General Electric Company, the possibility of using high pressure techniques to synthesize other new phases or produce materials with unique properties has been investigated. Several questions arise as to what effects might be anticipated from the use of high pressures in treatment of materials. Can new compounds or new phases be formed? Can equilibrium be shifted? Can structures be made more "perfect"? Can the kinetics of important transformations be changed?

Since the initiation of the Air Force program on high pressure metallurgy, many of these questions have been partially answered. However, before considering the above questions in detail, it seems appropriate to define terms used and to discuss the apparatus used to generate the high pressures simultaneously with temperature. The generally accepted unit of pressure is the kilobar; one kilobar is approximately equal to 14,700 psi. Most of the work which has been sponsored by the Air Force has been done at pressures between 30 kilobars and 100 kilobars, or 450,000 to 1,500,000 psi. It is obvious from the magnitude of these pressures that very few materials have strengths sufficient to withstand the lower pressure limit, let alone the higher pressure limit. Therefore, design tricks are employed to make the structural materials "think" they are operating at lower stress levels than they really are. A schematic of a high pressure device is shown in figure 3.

In principle, all that must be done is to exert a large force on a small area. In practice, this is achieved by employing tapered tungsten carbide pistons for the compressive components of the device and by using tungsten carbide cylinders held in compression by interference fitted tool steel rings for the tensile components of the device. Pressures of 100 kilobars are attained using proper gasketing to seal the pressure chamber and to provide lateral support for the relatively unsupported areas of the pistons. Heating is achieved by electrical resistance, using a cylindrical heating element within the pressure chamber, the heating current being introduced through the pistons. Thermocouples for temperature measurement are normally brought out through the gaskets between the piston and the cylinder. A typical cell is shown in figure 4. The dimensions of the cell are of particular interest; the diameter is only 0.35 inch and the length 0.45 inch.

It seems appropriate to mention that many precautions must be taken in the interpretation of results from high pressure experiments, but one of the most important of these is to separate the effects of hydrostatic pressure from those of the non-hydrostatic component which exists within most solid media cells, particularly upon application and release of pressure. The plastic deformation which may result from the application and release of pressure can markedly change the interpretation of results of high pressure experiments. Precautions must be taken to prevent sample contamination and to reproduce pressure and temperature accurately during a series of experimental runs. Inves-

tigators are forced to use small samples, in comparison to overall cell size, to minimize the effects of pressure gradients, temperature gradients, and contamination. For example, in the cell shown, the useful specimen size is approximately 0.15 inch diameter by 0.10 inch length. This small specimen size severely limits the type of evaluation tests that can be made on pressure treated samples. From this short discussion, the advantage of larger chamber volumes becomes apparent. However, increasing the chamber size is difficult and costly, particularly for cells to be used above 40 kilobars. Much apparatus development is necessary before high pressure will become an important materials development tool. An apparatus has recently been developed which will allow high pressure heat treatment of $\frac{1}{2}$ -inch diameter by 2-inch slugs up to 40 kilobars. This apparatus will allow much more complete evaluation of products than has been possible previously. We hope that even larger high pressure-high temperature apparatus will be available in the near future.

Now it seems wise to present some data which partially supplies answers to the questions previously raised regarding the potential of high pressure techniques in effecting new phase formation and changing equilibrium, crystal perfection, and transformation kinetics.

The synthesis of diamond, borazon (cubic boron nitride), coesite (a dense form of silica), and several minerals had illustrated the potential of high pressure techniques in producing new compounds before the Air Force program was initiated. Continued effort on compound synthesis has resulted in the production of a face-centered-cubic form of molybdenum monocarbide and the production of vitreous silica with a density almost as great as that of quartz, the most dense naturally occurring form of crystalline SiO_2 . An interesting plot of density vs. refractive index is shown in figure 5.

The vitreous phases of high density were produced by various combinations of pressure and temperature. We find that the vitreous materials of varying refractive indices may be produced from the same starting material by the application of pressure.

As might be expected, pressure has a profound effect upon phase equilibria in several metallurgically important systems. Since iron-based alloys have been extensively studied, they will be discussed here in detail. The transformation of ferrite (α -iron) to austenite (γ -iron) is of utmost importance to the ferrous metallurgist. Therefore, this transformation is a logical one to consider in this discussion on high pressure technology. Figure 6 shows that the effect of increasing pressure is to lower the transformation temperature. Thus, pressure tends to stabilize austenite, as might be expected from the decrease in volume observed when ferrite transforms to austenite. This stabilizing influence is further shown in the iron-chromium system and the iron-carbon system. Some of the metallurgical importance of these diagrams can be stated as follows: Iron-chromium binary alloys, which contain over 12 percent Cr, normally do not respond to heat treatment, since no phase transformation takes place upon heating (figure 7). However, by applying pressure during heat treatment, the $\alpha \rightarrow \gamma$ phase transformation may be induced in alloys of chromium content in excess of 12 percent, making these alloys, with their inherently good corrosion resistance, respond to heat treatment. Pressure has a similar effect on the Fe-Si and Fe-Al systems.

The iron-carbon system is familiar to materials engineers, and the changes such as shown in the diagram need very little interpretation (figure 8).

In essence, the effect of pressure upon the iron-carbon system is to decrease the solubility of carbon in austenite, decrease the eutectoid composition, and lower the eutectoid temperature. Thus, although the phases present after a high pressure heat treatment are

identical to the phases present after a one atmosphere heat treatment, the composition and distribution of these phases may be widely different. An interesting phenomena to note is the difference in the morphology of carbides precipitated by lowering the temperature and those precipitated by increasing the pressure. Figure 9 illustrates that carbides precipitated upon cooling tend to form as grain boundary aggregates, whereas those precipitated by an increase in pressure form as discrete particles within the grain. This phenomenon, if it extends to other systems, may be of considerable importance in cases where the formation of a brittle intergranular phase is undesirable. Iron-base alloys have been chosen as an example, since they are well known to most materials engineers; however, similar effects of pressure upon phase equilibria are noted in many other metallic, nonmetallic, and organic systems.

One of the most interesting areas of high pressure research in metallurgy is the effect of pressure upon transformation kinetics. In this area, the data obtained not only contribute to a better understanding of rate controlling mechanisms, but also may lead to superior materials for advanced systems. Again, it seems natural to use the iron-base alloys for purposes of comparison, since the one atmosphere kinetics are reasonably well known, and the transformation rates at high pressure have been quite thoroughly studied.

Of utmost importance in the heat treatment of steel is a knowledge of the hardenability of the specific alloy to be heat treated. Hardenability may be defined as "the property which determines the depth and distribution of hardness induced by quenching." In general, the higher the alloy content of a steel, the higher the hardenability. This increase in hardenability is reflected by a shift to the right in the isothermal transformation diagram. Pressure has an effect on the isothermal transformation diagram similar to the effect of increasing alloy content (figure 10). This diagram is for an iron-.75 percent C alloy, not for a plain carbon steel. An idea of the effect of pressure upon transformation kinetics in 1080 steel can be obtained from the isolated points on the diagram. Pressure is very effective in increasing hardenability when substitutional elements, such as the Mn found in 1080 steel, are present in addition to the interstitial carbon. The importance of this effect on hardenability is dramatically illustrated by the increase in hardness obtained in pressure treated plain carbon steels (table 1). The high hardness of the low carbon steel, is of particular interest. If such hardnesses can be consistently reproduced in larger specimens, steels with exceptional hardness plus the toughness normally associated with lower carbon steels may be produced.

Another pressure effect of importance to steel metallurgy is the retarding of tempering by the application of pressure. This is graphically shown in figures 11 and 12 as the difference in hardness between iron-carbon alloys tempered at various temperatures at one atmosphere and at 42 kilobars.

From isothermal studies made on several systems, including Fe-C, Al-Cu, Cu-Be, Pb-Sn, and Au-Ni, we found that one pressure effect was common to all. In every case, the application of pressure retarded the rate of isothermal transformation; however, the changes in rate vary from a factor of 4 to a factor of over 400. The decrease in rate depends on many factors, including whether or not nucleation, interstitial diffusion, substitutional diffusion, bulk diffusion, or grain boundary diffusion is the rate controlling factor.

The last factor to consider is crystalline perfection. Is it possible, by heating a solid under pressure, to drive out dislocations, giving a structure of theoretical strength? Data obtained thus far indicate that although the application of pressure may energetically favor the annihilation of dislocations, the mobility of these defects is so reduced by the

pressure that no overall reduction in dislocation concentration is observed. This effect is shown in figure 13. No conclusive evidence has been produced which would indicate that a material solidified under pressure has fewer dislocations. The marked reduction in the rate of substitutional diffusion at high pressures does, however, indicate a reduction in vacancy concentration as a result of pressure treatment. Therefore, the application of high pressure to solids results in a reduction of the number of point defects but has very little effect on the number of line defects.

From the discussion of static high pressure apparatus, we find that the ultimate size of parts to be treated will always be limited. Such is not the case if the pressures are generated dynamically by explosive, spark discharge, or other techniques. Explosive forming is well known and is being widely exploited, but the hardening produced in metals by the passage of a strong shock wave is relatively unknown. This hardening can be realized even though the sample is not deformed. Commonly, the curve of hardness vs. shock pressure shows a continuous increase in hardness with pressure such as the curve for columbium in figure 14. However, the same curve for iron shows a sharp change in slope at 130 kilobars. This change in slope corresponds with the transformation observed by Bancroft, as indicated above in figure 6. The exact nature of this transformation is not known, but the volume change observed is very similar to the volume change involved in the transformation. A marked discrepancy exists between the pressure at which the shock induced transformation takes place at room temperature and the pressure at which the $\alpha \rightarrow \gamma$ transformation should take place according to thermodynamic calculations which have been applied successfully to static measurements of the $\alpha \rightarrow \gamma$ transformation up to 80 kilobars. Much work remains to be done on the mechanism of this transformation of iron, but the possibilities of utilizing the transformation for hardening purposes should be investigated immediately. It is the purpose of two Air Force sponsored programs to investigate this possibility, and to utilize shock as a means of imparting energy into "metastable" phases prior to final heat treatment.

One more unique technique which warrants mention here is the ultra rapid cooling ("splat" cooling) technique developed by Duwez and co-workers. Extremely rapid cooling rates are achieved by impinging a small droplet of the alloy on the inside wall of a rapidly rotating copper drum. The alloy is deposited as a thin film which is held tightly against the drum by centrifugal force. As a result of the rapid cooling achieved, Duwez et. al. have observed completely new structures in binary and pseudo binary systems. The type of result obtained is shown schematically in figure 15. Here, the silver-copper system is shown as a simple eutectic. When a complete series of Ag-Cu alloys is "splat" cooled, a series of solid solutions is formed. The lattice parameters obtained from these alloys, fall on a smooth curve connecting the two previously known segments which lie within the solubility limits at both ends of the equilibrium diagram. Similar behavior is observed in the germanium-gallium antimonide pseudo binary system. In other systems, for example Ag-Ge, compounds are formed in regions where only terminal solid solutions previously existed.

Presently, the Air Force is attempting to use "splat" cooling techniques to study certain selected beryllium rich binary systems in an effort to gain a more complete understanding of the alloying characteristics of beryllium. This program may also produce new materials with unique properties, for use in advanced systems, although with the present state of the art of ultra rapid quenching, such materials could be formed only as small, ultra thin foils.

In summary, the Air Force is investigating unique materials and techniques with the hope that such investigations may lead to quickening strides in materials technology. The

materials investigated have included beryllium, scandium, yttrium, and the rare earths. The techniques employed have included application of high static and dynamic pressures and ultra rapid quenching. Admittedly, the probability of success in some of these programs is low; however, the necessity for rapid gains in materials technology makes some effort in these areas highly desirable.

BIBLIOGRAPHY

1. Claussen, W. F., Devries, R. C., and MacKenzie, J. D., "The Influence of High Pressures and High Temperatures on Transformations and Coordination in Crystalline and Vitreous Ceramic Materials," WADD Technical Report 60-304, November 1960.
2. Dieter, G. E., "Metallurgical Effects of High-Intensity Shock Waves in Metals," Response of Metals to High Velocity Deformation, Metallurgical Society Conference, Interscience, New York.
3. Duwez, Pol., Willens, R. H., and Klement, W. Jr., "Metastable Solid Solutions in the Gallium Antimonide-Germanium Pseudobinary System," Journal of Applied Physics, Vol. 31, No. 8, 1500, August 1960.
4. Duwez, Pol., Willens, R. H., and Klement, W. Jr., "Continuous Series of Metastable Solid Solutions in Silver-Copper Alloys," Journal of Applied Physics, Vol. 31, No. 6, 1136-1137, June 1960.
5. Duwez, Pol., Willens, R. H., and Klement, W. Jr., "Metastable Electron Compound in Ag-Ge Alloys," Journal of Applied Physics, Vol. 31, No. 6, 1137, June 1960.
6. Goliber, E. W., McKee, K. H., Kasper, J. S., Hilliard, J. E., Cahn, J. W., and Phillips, V. A., "Research and Development on the Effects of High Pressure and Temperature on Various Elements and Binary Alloys," WADC Technical Report 59-747, July 1960.
7. Harvey, J. S., Kaufman, L., Kulin, S. A., Leyenaar, A., and Udin, H., "Research and Development on the Effects of High Pressure and Temperature on Various Elements and Binary Alloys," WADC Technical Report 59-655, April 1960.
8. Hilliard, J. E., "The Effect of Pressure Upon Phase Equilibria and Diffusion Rates in the Iron-Carbon System," ASD Technical Report 61-21 Part I (to be published).
9. Kaufman, L., Radcliffe, S. V., Kulin, S. A., Shatz, M., Kafalas, J., Tanner, L., Bernstein, H., Leyenaar, A., and Harvey, J. S., "Research and Development on High Pressure-High Temperature Metallurgy," WADD Technical Report 60-893 (to be published).
10. Love, B., "Selection and Evaluation of Rare or Unusual Metals for Application to Advanced Weapons Systems - A Literature Survey," WADC Technical Report 57-666 Part I, June 1958.
11. Love, B., "Selection and Evaluation of Rare or Unusual Metals - The Metallurgy of Yttrium and the Rare Earth Metals," WADC Technical Report 57-666 Part II, March 1959.

12. Love, B., "The Metallurgy of Yttrium and the Rare Earth Metals - Phase Relationships," WADD Technical Report 60-74 Part I, May 1960.
13. Love, B., "The Metallurgy of Yttrium and the Rare Earth Metals - Mechanical Properties," WADD Technical Report 60-74 Part II, June 1960.
14. Love, B., "The Technology of Scandium, Yttrium, and the Rare Earth Metals - A Literature Survey," WADD Technical Report 60-864 (to be published).
15. Love, B., "The Metallurgy of Yttrium and the Rare Earth Metals," WADD Technical Report 61-123 (to be published).
16. Progress in Ultra High Pressure Research - Proceedings of an International Conference held at Bolton Landing, Lake George, New York, on 13-14 June 1960, WADD Technical Report 60-464 (to be published).

Table 1

STEEL	VICKERS HARDNESS		(100 gm Load)
	PRESSURE HEAT TREATMENT 3 9 Kb	ONE ATMOSPHERE HEAT TREAT	
0.4 C	1050	625	
0.8 C	925	700	
1.1C	940	675	

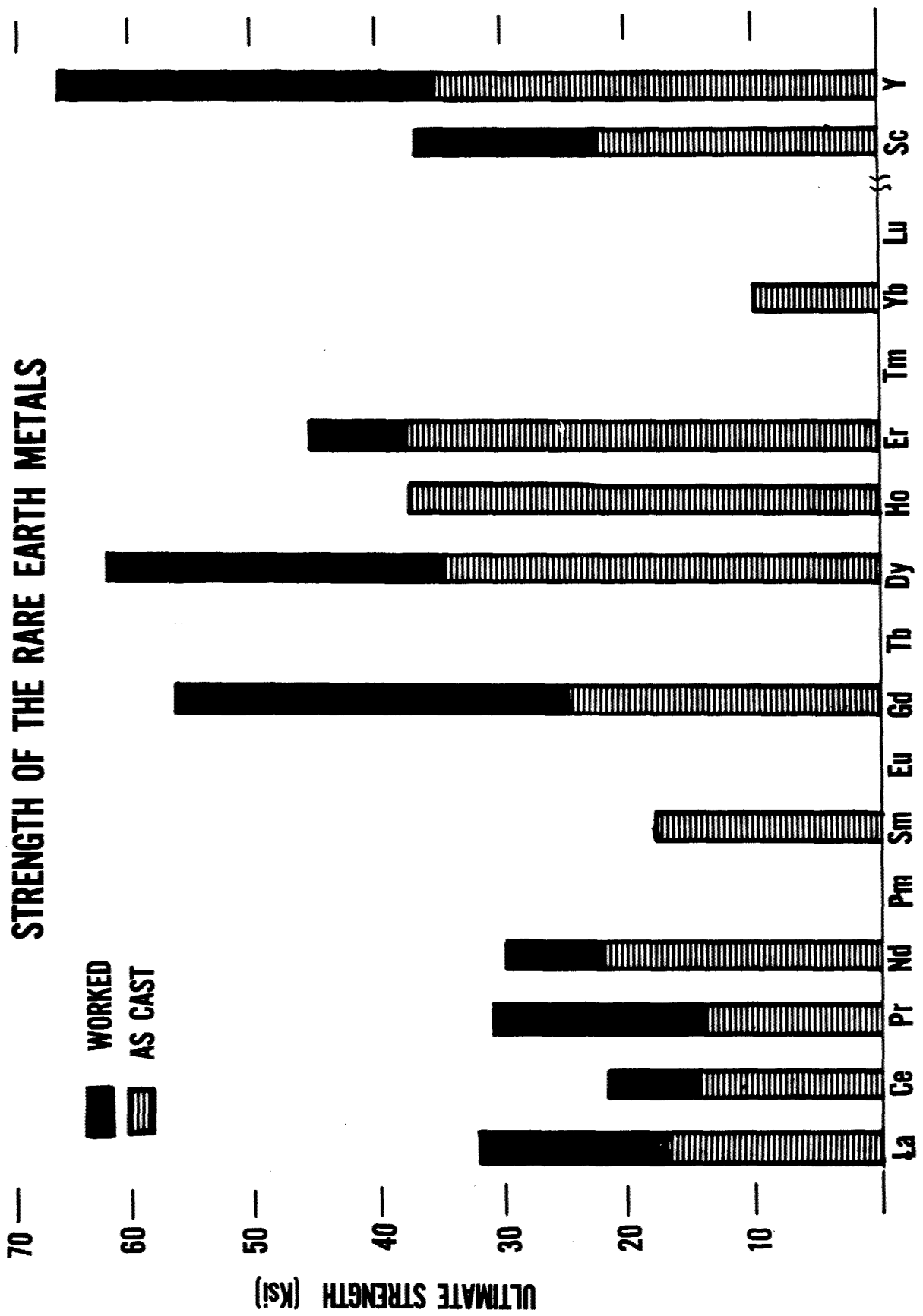


Figure 1.

ATMOSPHERIC CORROSION OF THE RARE EARTH METALS IN DRY AIR AT 750°F

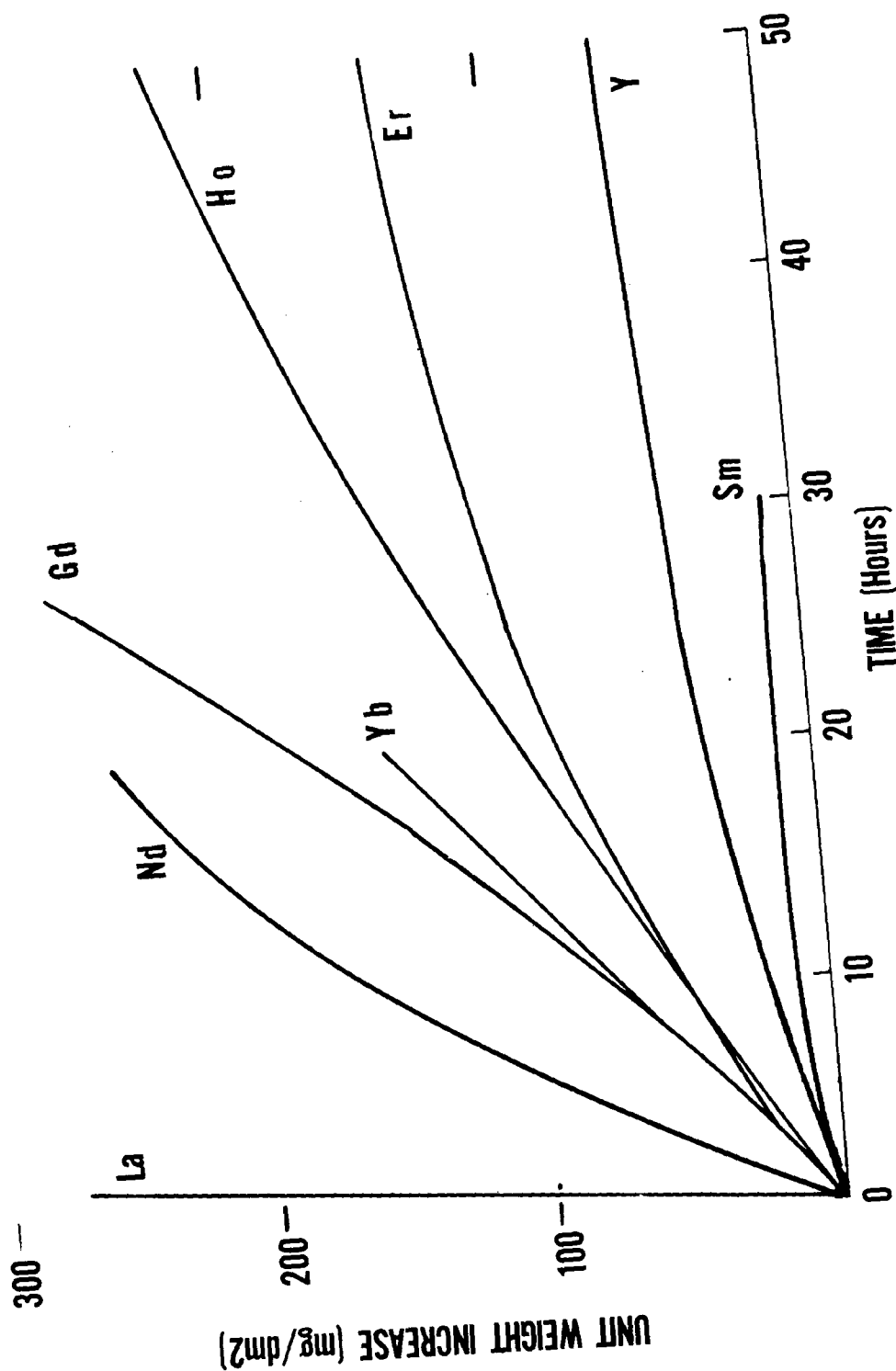


Figure 2.

THE BELT APPARATUS

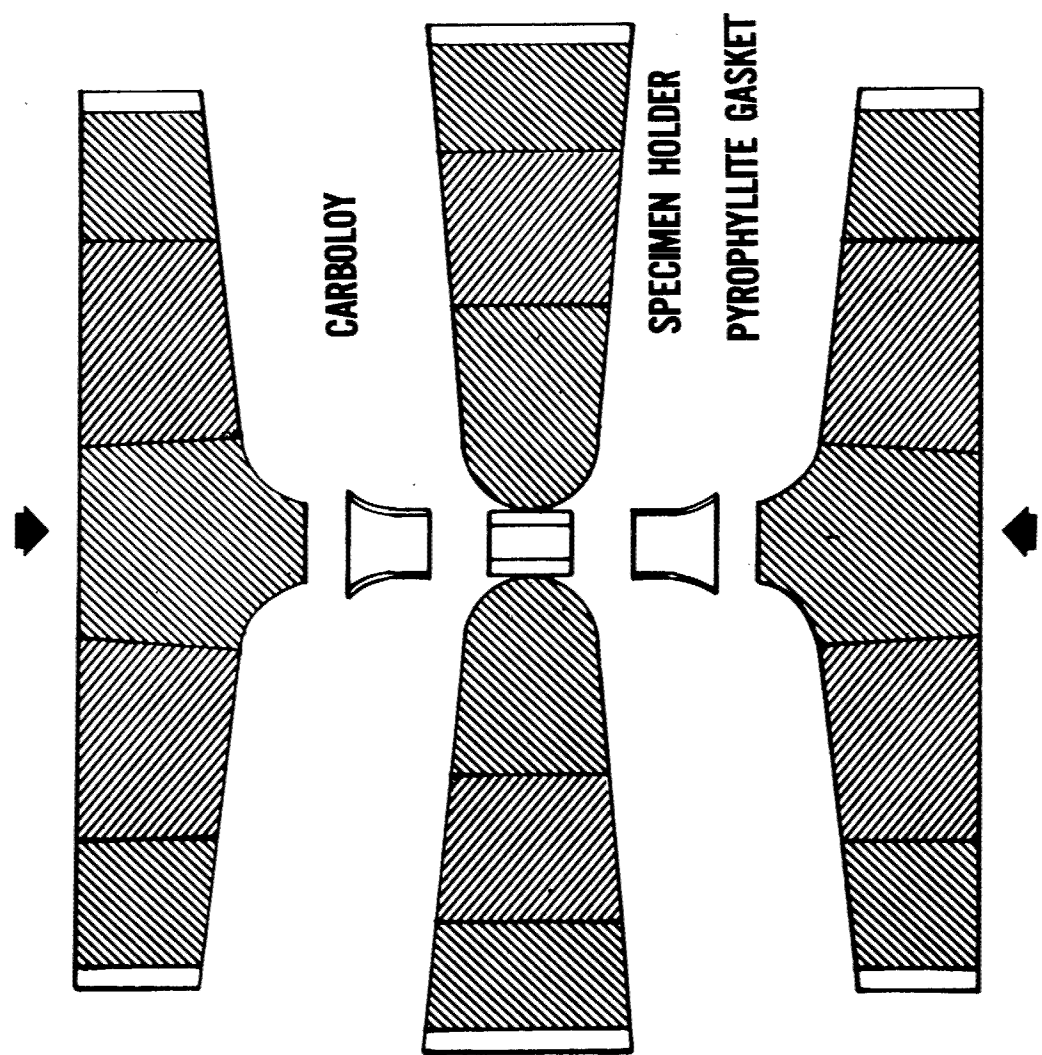


Figure 3.

A TYPICAL HIGH PRESSURE CELL

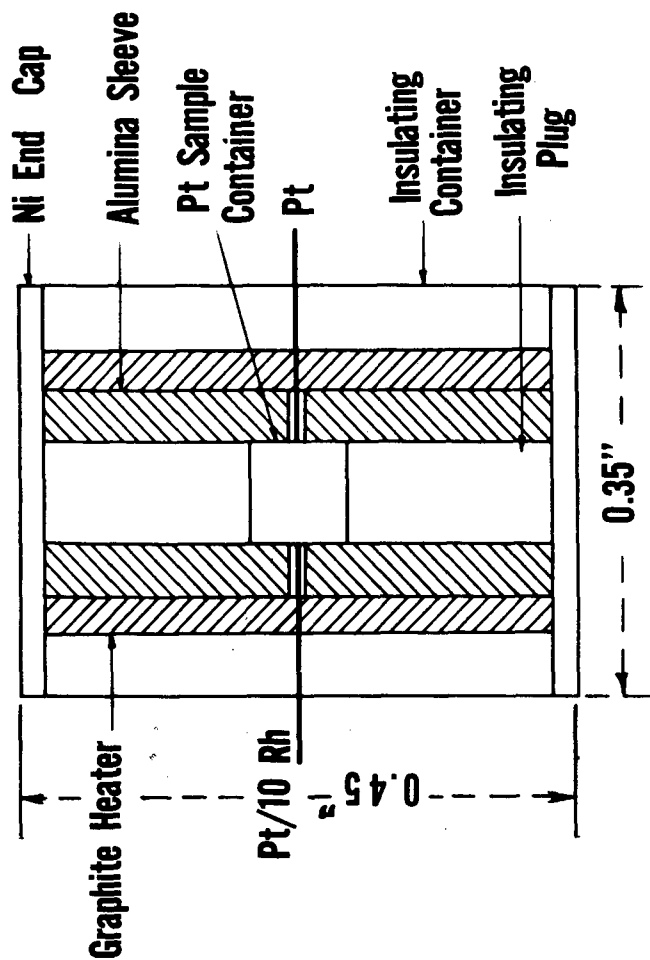


Figure 4.

REFRACTIVE INDEX—DENSITY RELATIONSHIP FOR SiO_2

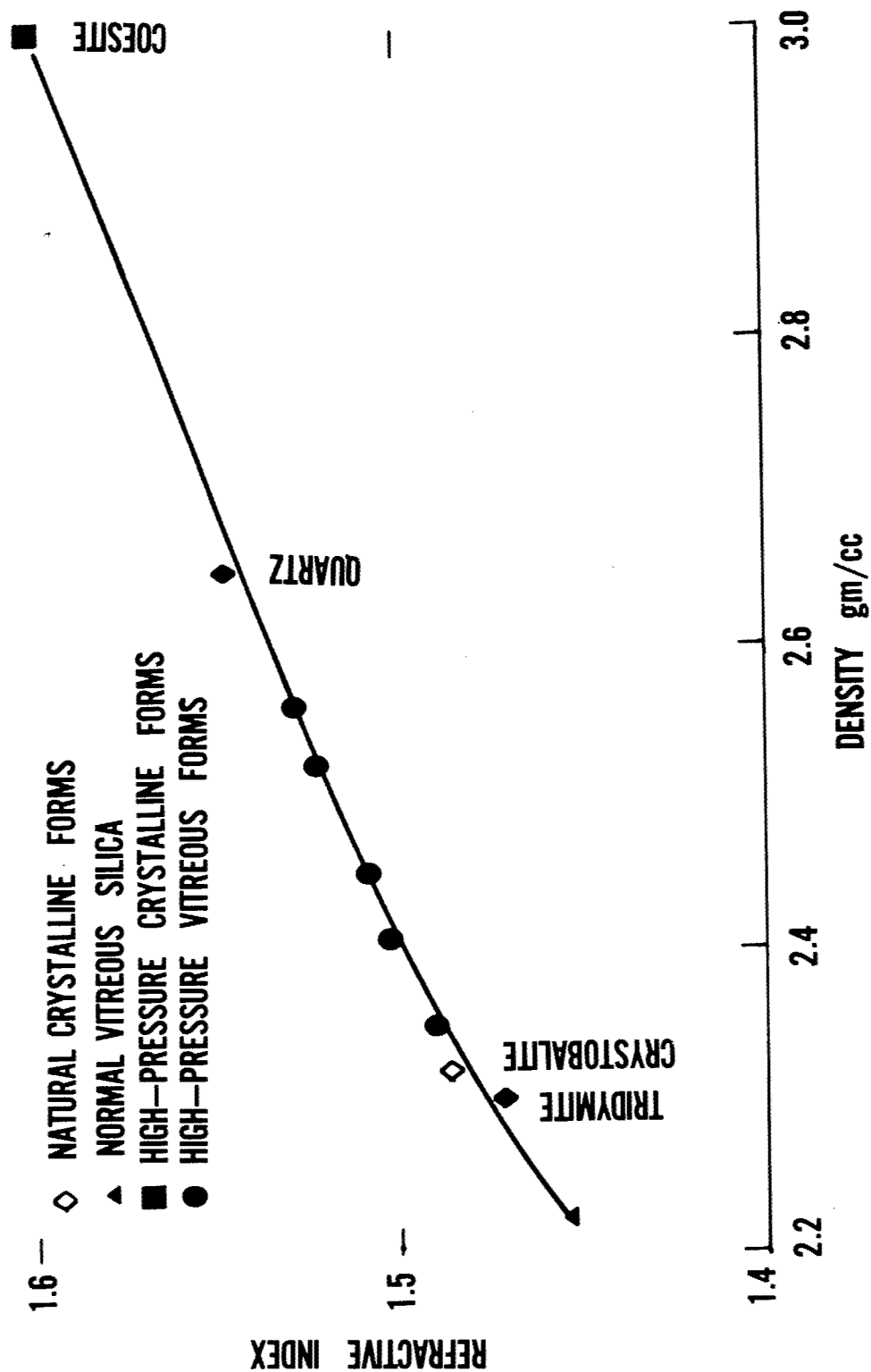


Figure 5.

EFFECT OF PRESSURE ON THE $\alpha \rightarrow \gamma$ TRANSFORMATION IN IRON

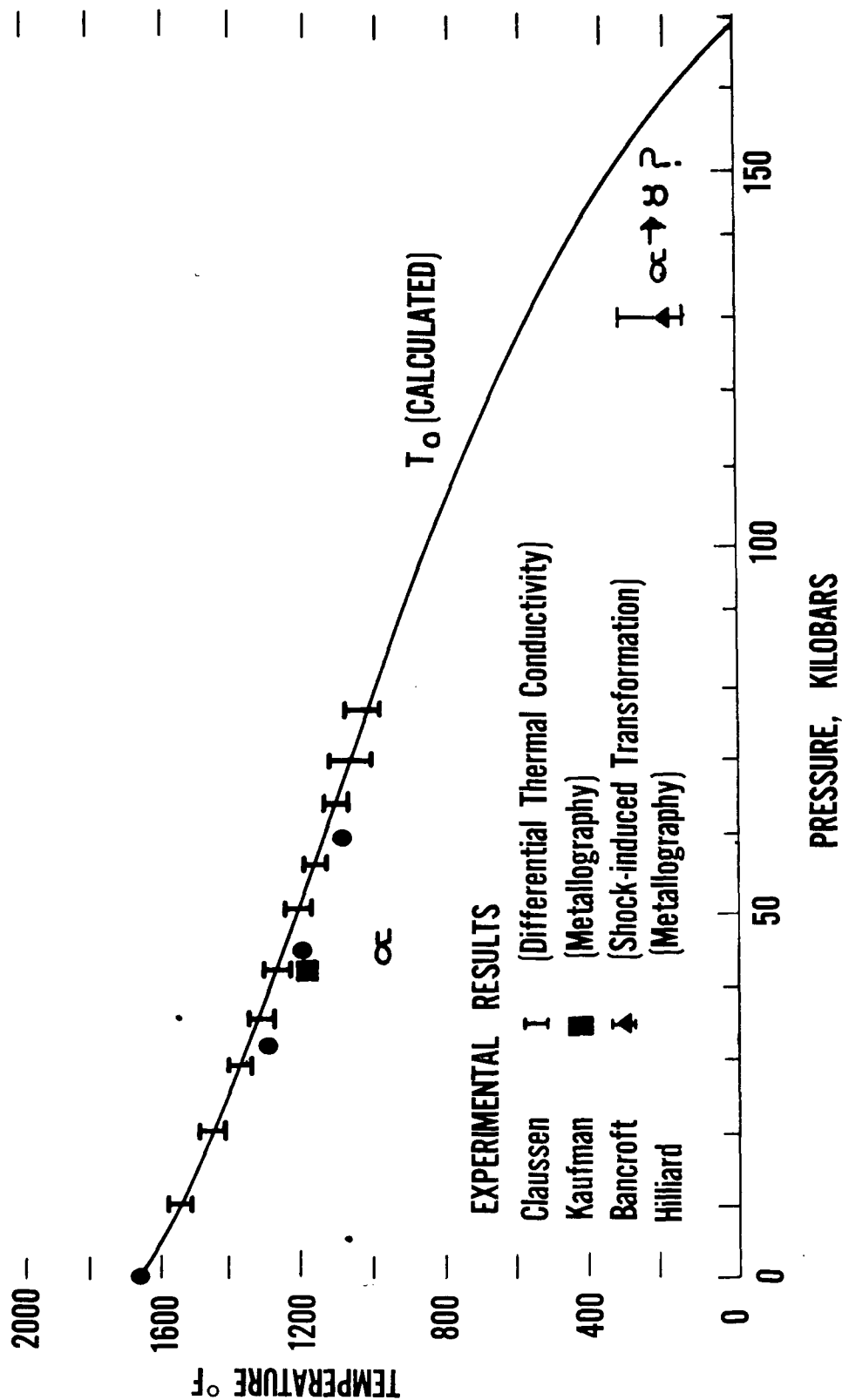


Figure 6.

THE IRON—CHROMIUM SYSTEM

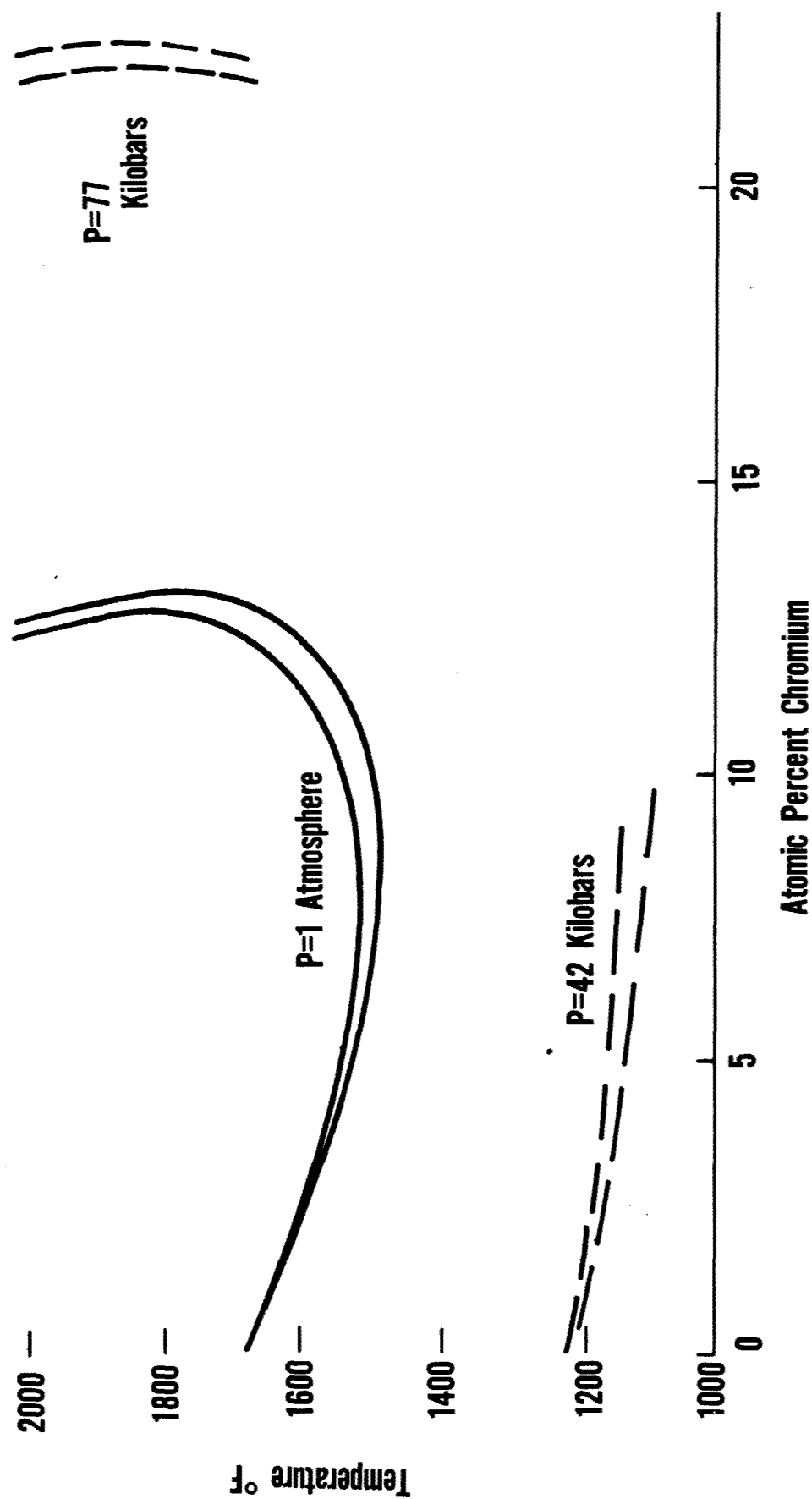


Figure 7.

THE IRON-CARBON DIAGRAM

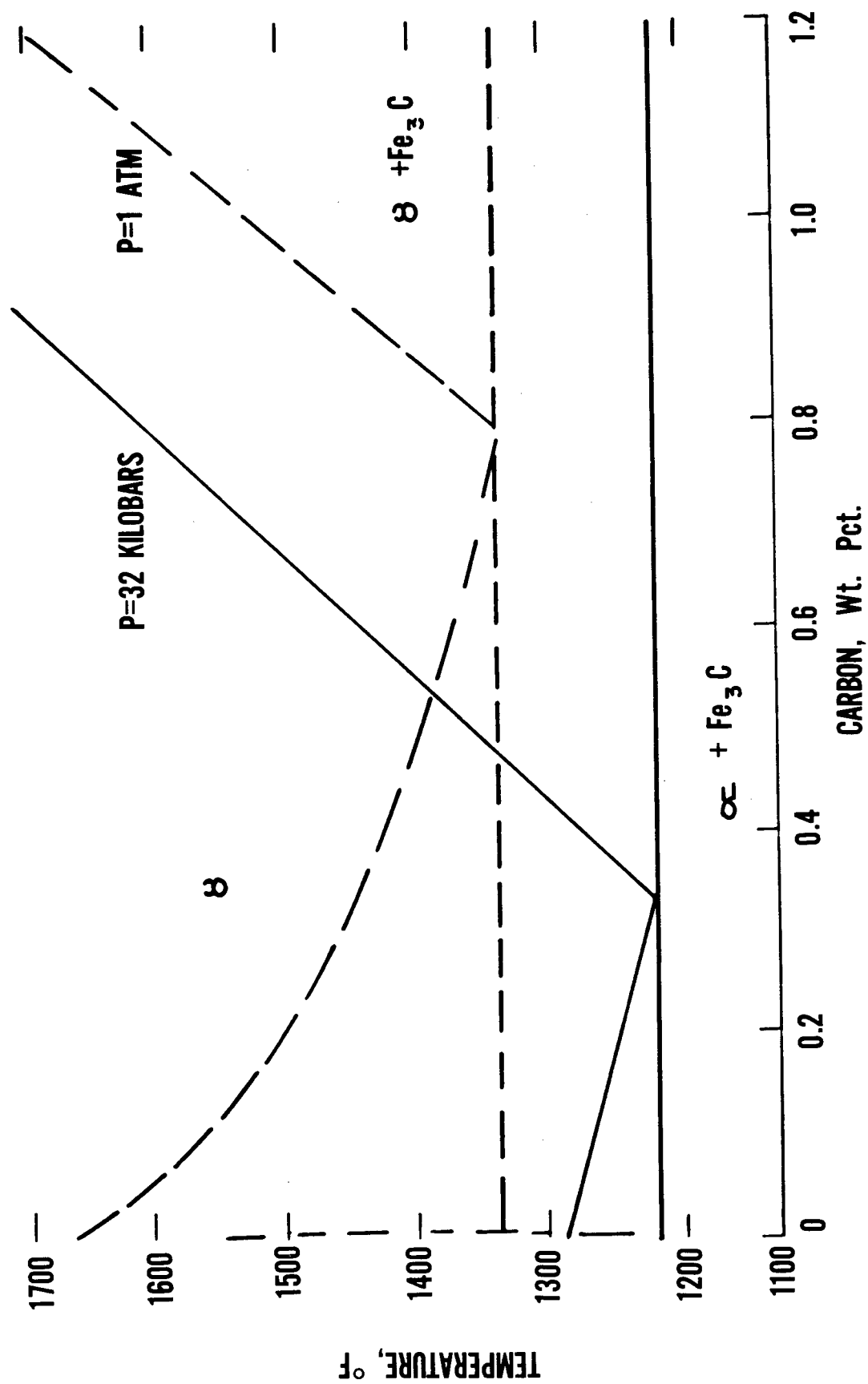
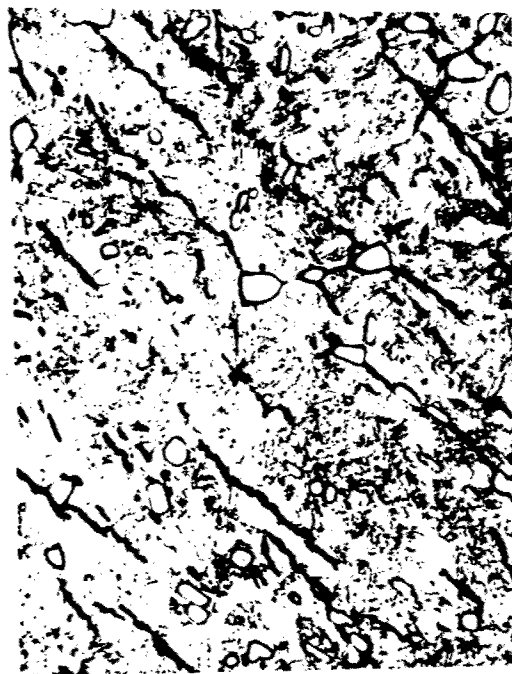


Figure 8.

CHANGES IN CARBIDE MORPHOLOGY



**CARBIDES PRECIPITATED BY
INCREASING PRESSURE**



**CARBIDES PRECIPITATED BY
DECREASING TEMPERATURE**

Figure 9.

ISOTHERMAL TRANSFORMATION DIAGRAM FOR AN IRON-0.75% CARBON ALLOY

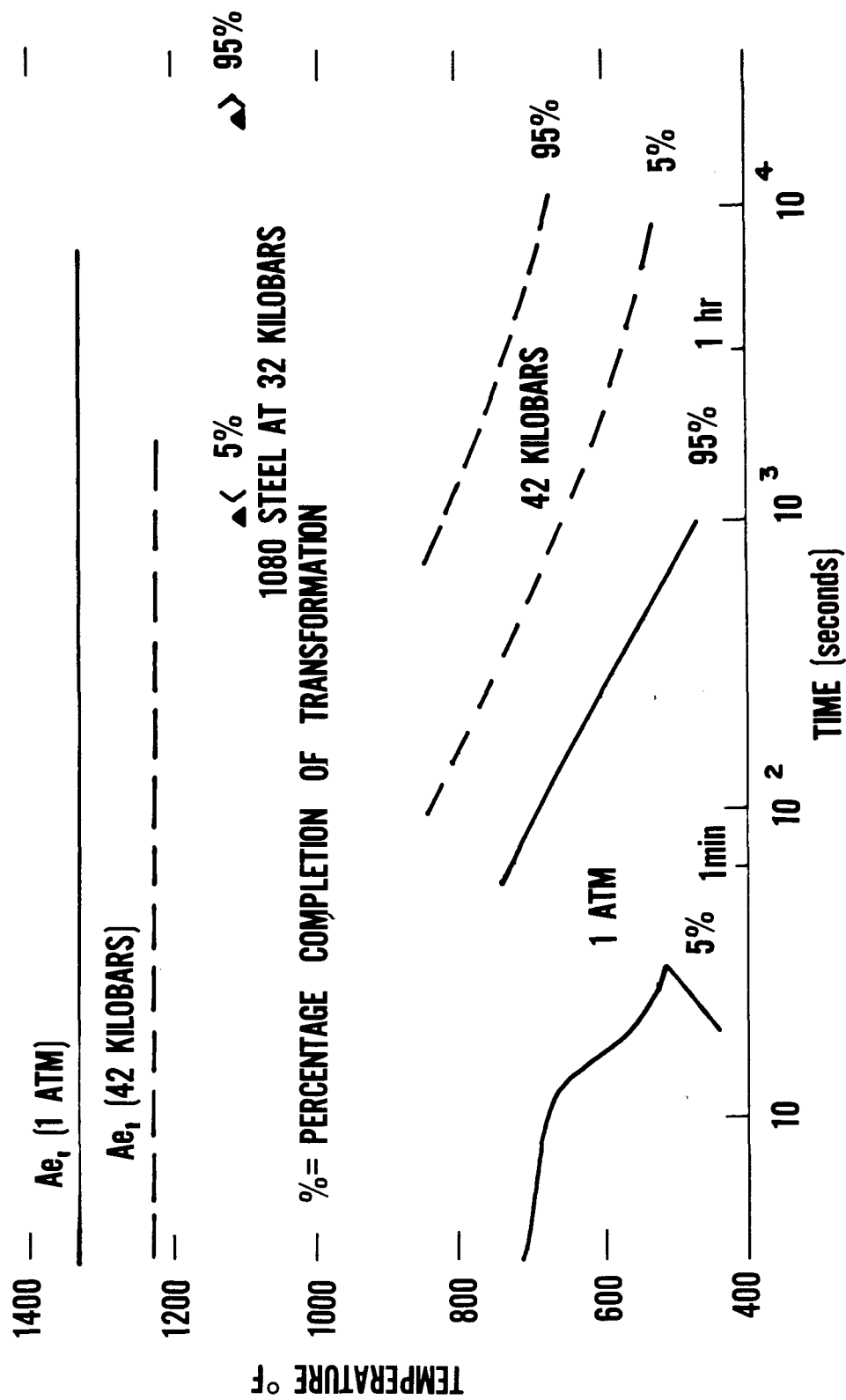


Figure 10.

HARDNESS DIFFERENCE BETWEEN IRON—CARBON ALLOYS, TEMPERED AT 1 ATM AND 42 KILOBARS

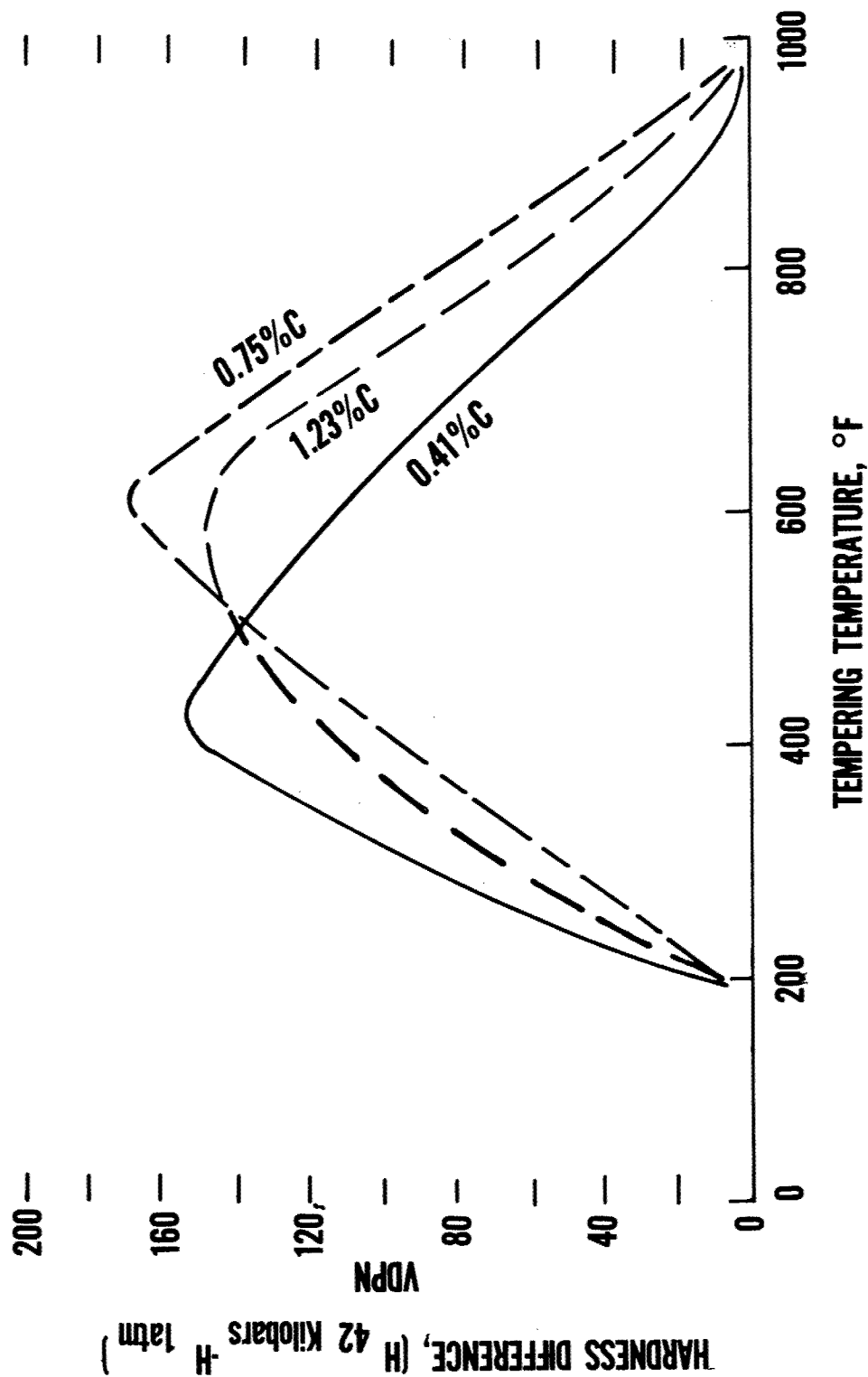


Figure 11.

AS-TEMPERED HARDNESS, OF AN IRON-0.41 WT % CARBON ALLOY

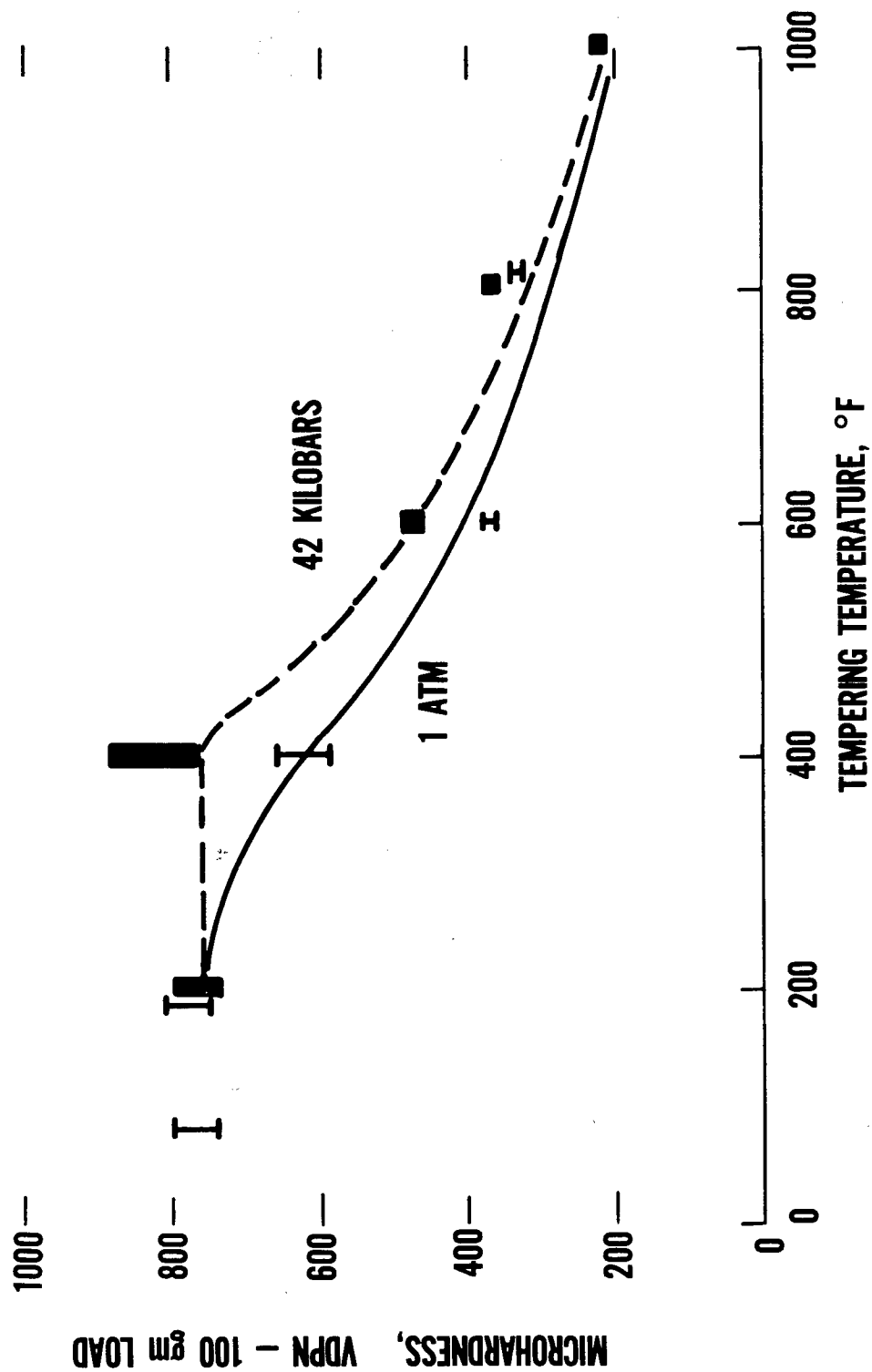
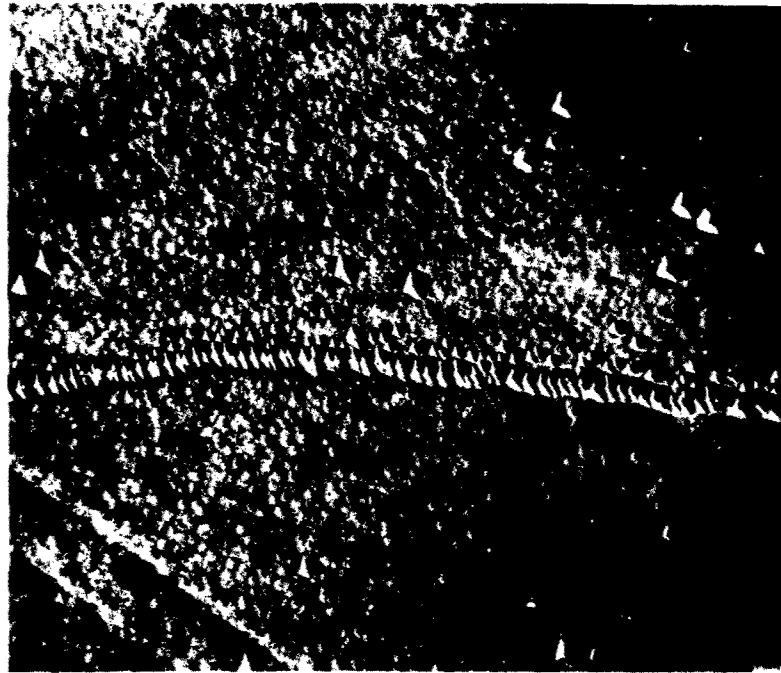


Figure 12.

MATCHING CLEAVED SURFACES OF A LIF CRYSTAL



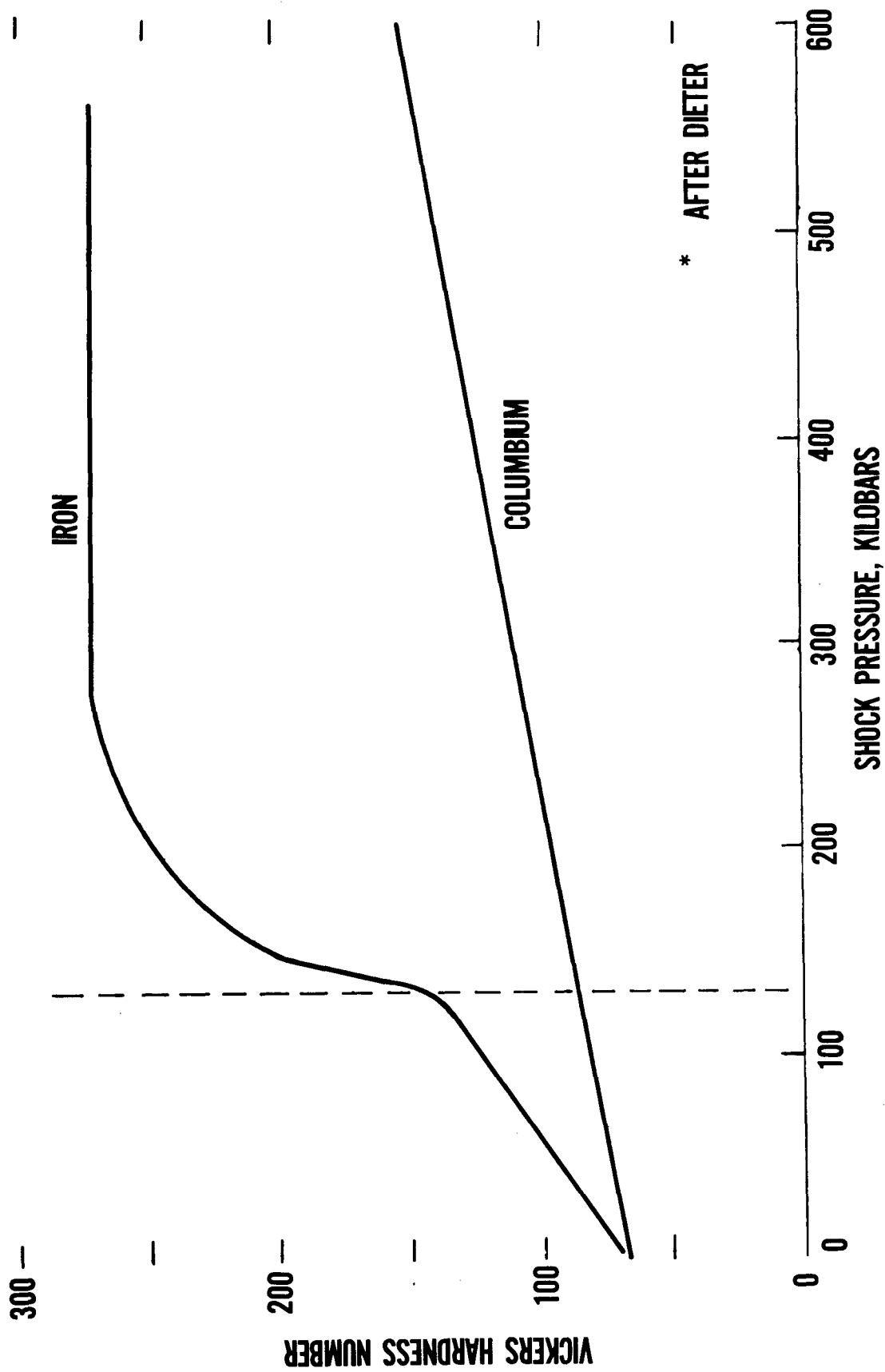
Annealed 1 hr at 932° F and 40 Kilobars



**Annealed 1 hr at 932 ° F
at atmospheric pressure**

Figure 13.

HARDNESS vs. SHOCK PRESSURE FOR IRON AND COLUMBIUM*



* AFTER DIETER

Figure 14.

SCHEMATIC REPRESENTATION OF THE Ag—Cu SYSTEM

586

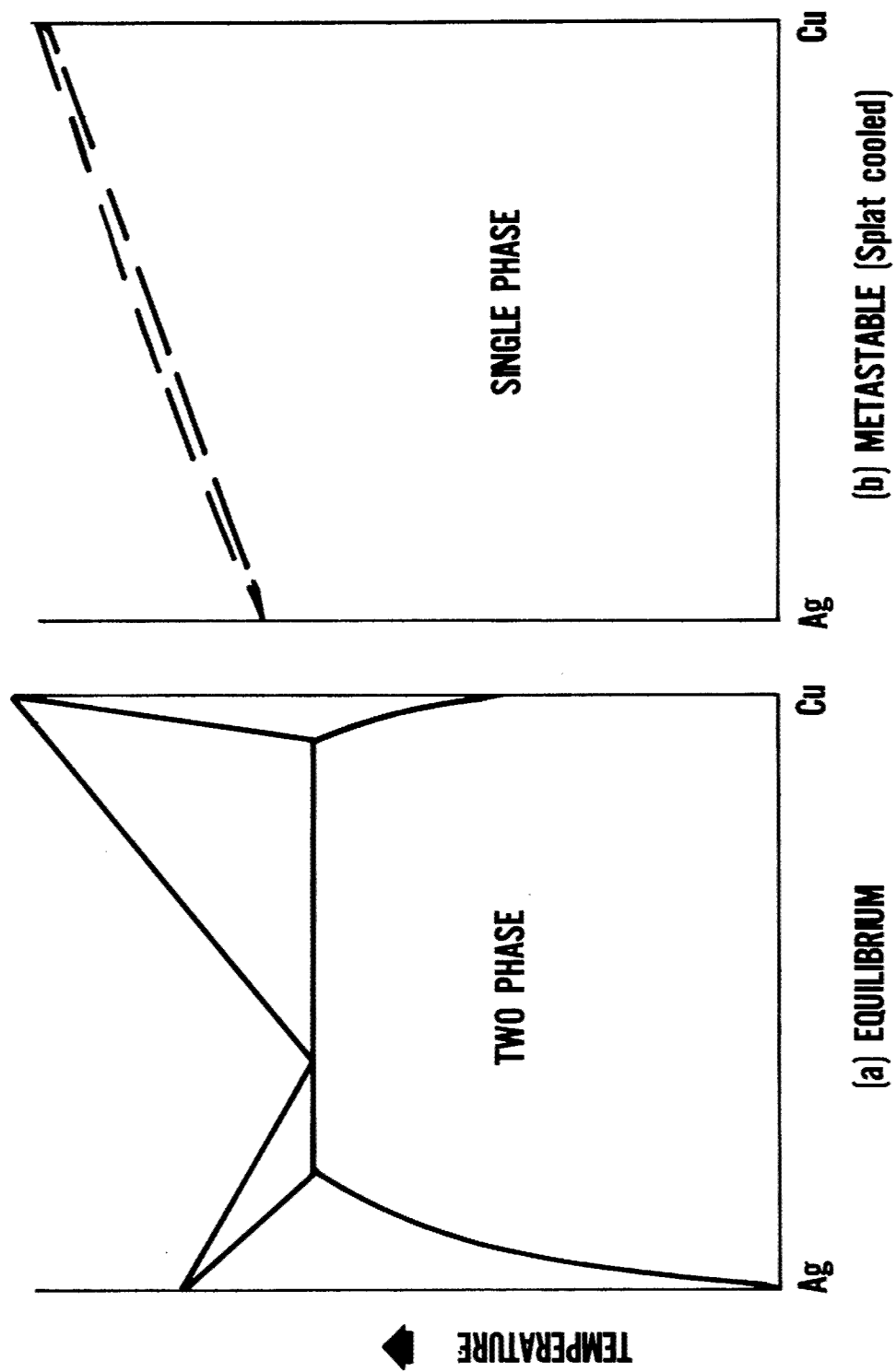


Figure 15.

MATERIALS FOR ENERGY CONVERSION

Chairman

Mr. B. Rubin

Speakers & Panel Members

Mr. G. E. Thompson

Capt. E. F. Redden

Mr. R. W. Runnels

Mr. B. Rubin

MATERIALS PROBLEMS IN DYNAMIC ENERGY CONVERSION SYSTEMS

George E. Thompson

Directorate of Aeromechanics, ASD

Introduction

To present a brief review of some of the fundamental design and material problems involved in the successful development of a dynamic space power system is the purpose of this paper. This brief review should assist in stimulating discussions on the nature of the problems, methods of solution, and the degree of emphasis required in the solution of particular problems.

In an effort to cover such a broad subject, a quantitative approach is used and two specific examples, namely collectors and radiators, are selected to further illustrate some fundamental design and material problems.

Dynamic Energy System

Figure 1 illustrates schematically a typical dynamic energy conversion system. Heat is added to the working fluid in the boiler or heat exchanger by either a nuclear or solar heat source. The high thermal energy in the high pressure fluid is transformed into kinetic energy, through nozzles, and partially transformed in the turbine to mechanical shaft power. The remaining energy is rejected from the system by cooling the lower pressure and temperature working fluid in the radiator-condenser. The working fluid is brought back to initial pressure by either a pump or compressor. Basically, either a two phase fluid in a Rankine cycle or a single phase fluid in a Brayton cycle is used in a dynamic energy conversion cycle.

Specific drawbacks of the Rankine cycle include corrosion and mass transport characteristics with the use of liquid metal as a working fluid, turbine blade erosion due to a partial two-phase fluid, phase changes occurring under the absence of gravitational force, and the pressure drops occurring during the phase changes. These severely penalize proper cycle operations.

Solar Dynamic System

From a series of design studies of dynamic energy conversion systems with various power levels, akin to the rubber engine concept in propulsion, the relative contribution of individual components to the overall design problem may be studied. Thus, the relative contribution to the weight of a range of solar dynamic power systems is shown in figure 2, for major components.

Three components, collector, energy storage, and radiator, increase in percentage weight with power output. Two components, the boiler and turbine-pump, decrease in percentage weight, with power output. Great care should be exercised in reading this plot. A maximum cycle temperature of 1200°F was assumed. This allowed the use of lithium hydride as an energy storage material (approximately 1100 btu/lb are available as latent heat).

An increase in cycle efficiency is most readily achieved by an increase in temperature differential and/or temperature level (i.e. increase in maximum cycle temperature). The increase in cycle efficiency will greatly benefit the collector. If an increase in cycle efficiency is achieved by an increase in maximum cycle temperature, the new energy storage material will now be either sodium fluoride (350 btu/lb latent heat), beryllium (450 btu/lb), or silicon (550 btu/lb). The decrease in latent heat capability coupled with the increase in material density may result in a system design where the percentage weight of the energy storage device equals or even exceeds the percentage weight of the collector.

Let us select the collector component and review some of the design considerations which have a bearing upon materials requirements.

Collector Design Considerations

The parameters encountered in designing a solar collector are primarily mechanical. Surface finishing, geometric accuracy, concentration ratio, reflectivity, boiler absorptivity and emissivity, solar constant, and overall system efficiency play a predominant part in arriving at the collector area required for a solar powered space system.

In order to achieve a usable temperature at the boiler surface, the low space solar density is amplified by means of concentration. Figure 3 illustrates the effect of concentration ratio, defined as the ratio of projected collector area to target-boiler area, on design considerations of solar collectors. Plotted on this slide we have the collection efficiency, versus boiler temperature, with the concentration ratio as parameter. To obtain reasonably high operating temperatures for improved overall efficiency, a high concentration ratio is necessary.

Material conditions have a pronounced effect on the concentration capability of large collectors. Imperfections introduced in the manufacturing of collectors may be classified as either geometrical errors or surface finishing errors. The possibility of producing geometrical errors is rather high, especially for collectors of 30 to 60 feet in diameter. Any large surface may deviate from an ideal geometry in a number of ways. Errors such as surface ripples, overdishd or flattened profiles, will result in a reduction of collector performance. The existence of ripples will generally cause a spread of the focal region. The over-dished or flattened profiles will result in a variation of the focal length. The factors directly involved in the control of geometrical errors are the type of construction and the method of manufacturing. Commonly considered types of construction are the rigid deployable with very light weight metal or honeycomb petals and the inflatable plastic type (e.g. mylar) rigidized with a foamed plastic. The materials and type of construction have a great bearing upon how extensively temperature gradients effect geometrical accuracy. An analytical assessment of geometrical errors is rather difficult and must be substituted by a cumbersome and costly experimental checkout. Surface finishing errors include the roughness of the base material and the surface roughness errors introduced by coating the base material. The majority of these errors will tend to create a beam spread or a dispersion effect which will seriously reduce the overall collection efficiency.

Nuclear Dynamic System

Figure 4 represents the variation in weight of the components of a nuclear dynamic power system as a function of power output. A two loop system using lithium in the primary loop and potassium in the secondary loop with a turbine inlet temperature of 1900°F and a condenser temperature of 1340°F is assumed in figure 4. The system does not include the penalty involved with subcooling for lubricating both the alternator and bearings.

As you can observe, the weight of the radiator and alternator increase with power output. The weight of reactor and shield decrease with power output. The weight of the turbo-heat exchanger is approximately constant with power output.

Let us now select the radiator component and review some of the design considerations.

Radiator Design Considerations

Both internal and external parameters dictate the design of a space radiator. Factors involved in the design of a radiator include: system configuration, whether direct or indirect condensation is selected; the internal heat transfer coefficients; allowable pressure drops; fluid velocity; corrosion; zero gravity operations; tube diameter; wettability of fluids; flow stability; tube-fin combination; fluid and material temperature drops; properties of materials; coatings; allowable configuration (flat plate, cylinder, etc.); and external environmental factors.

The necessity of operating at elevated temperatures necessitates the use of liquid metals as either working fluids or cooling fluids. Liquid metals are very corrosive, and their corrosion rate is very sensitive to the operating temperatures, and temperature differential. High-strength materials, such as the stainless steel series and Haynes 25 will find limited use in nuclear dynamic systems. Refractory materials, for example columbium, will also be required.

The importance of internal design considerations is illustrated in figure 5. Allowable pressure drops have to be kept to a minimum since at the operating temperatures, the pressure level of liquid metals is rather low. This restriction, combined with the absence of gravity, may severely restrict the actual value of the film coefficient. The variation in radiator area required as a function of radiator temperature with the film coefficient as parameter is illustrated in figure 5.

Operational and External Environmental Considerations

In addition to the internal environmental and design considerations for evolving the components of an integrated energy conversion system, there are external environmental and operational considerations which will have a strong influence. (figure 6).

Meteoroids

Possible harmful effects of meteoroids are as follows:

- a. May penetrate radiator tube wall resulting in either a puncture with a loss of working fluid or, at a minimum, a structural weakening of that particular component.
- b. May erode surface finishings, therefore changing radiator surface emissivity and collector optical characteristics. In order to design properly the components affected by meteoroids, it is imperative that the design engineer has some knowledge of the properties of meteoroids, their frequency of occurrence, mass, and size distribution, their velocity distribution, an analytical and/or empirical description of impact phenomena at the hypervelocities encountered.

Radiation

The low thermal efficiencies of dynamic space power systems requires the removal of approximately 80 to 90 percent of all the heat generated in the power plant. The vacuum in space necessitates the use of radiation mechanism as the sole heat removal possibility for long duration systems. To reduce exposure of critical areas such as radiator tubes to meteor penetration, fins will be employed dividing the heat load between the tubes and the fins.

The radiator area varies inversely with the emissivity of the surface. In view of the low emissive capability of bare metals, coatings are employed; however, every care must be taken that the right coating is selected for each component. For example, for radiators high emissivity is desired in the infrared region, but low absorptivity at the solar wavelengths.

High Vacuum

Perhaps the most critical question is that of stability. Will the selected materials and coatings last (1 to 2 years), the duration of the powerplant?

Reliability

A maximum reliability is obviously desired. Replacement of minor parts, although not impossible, should be kept to an absolute minimum. The major problem here is how to achieve maximum reliability with minimum penalty from both an operational and weight standpoint.

Weight and Volume

A minimum of both is desirable and will generally be achieved with an increase in cycle operating temperatures requiring a maximum of new material development. The working fluids will be of the liquid metal class where problems of corrosion, erosion and mass transport are very severe.

Perhaps the most critical design consideration for both radiator and collector is the question of space meteoroids, critical in the sense that this design criteria may very well dictate whether a large area component is possible. Three major design considerations need to be explored. First, what is the distribution of space meteoroids? Second, what is their frequency? Third, what is the damage caused by a meteoroid? Factors of importance in the distribution of meteoroids include size, velocity, and density. Upon the establishment of velocity, density, and mass distribution, the meteoroid flux will establish the number of hits per unit area per unit time. Damages caused by meteoroids cover possible loss of working fluids from penetration and spalling of tubes. Design possibilities to overcome meteoroid damages include the use of fins, bumpers, segmentation, all of which increase the temperature drop throughout the radiator. An increase in survival probability will cause a tremendous increase in weight. For example, an increase in probability of 0.9 to 0.999 will cause a five-fold increase in weight.

In order to reduce vulnerable area, non-fluid radiators have been proposed. A schematic is illustrated in figure 7. The fluid to be condensed is maintained in either a stationary or rotating fluid manifold. A moving belt is forced to contact the manifold; the heat is transferred by conduction. As the belt rotates through free space, the temperature decreases by radiation. Therefore, a continuous heat transfer process through

contact with the fluid manifold is insured. Only the manifold in this case must be protected from meteoroid damage. The belt could be made very thin, thus realizing the lower weight system. Crucial material problems involved here are emissive coatings that will operate not only in a high vacuum, but under a variable temperature; seizure problems in high vacuum accompanied with extreme temperature differential and high contact pressure, internal heat transfer; and possible seal problems.

Summary and Conclusions

The problems outlined herein do not constitute all of those present in dynamic power systems. This discussion has included detailed materials problems for two of the major components, namely: solar collector and thermal radiator. Similar discussions can be put forth for the remaining critical components, including heat exchanger-radiators, thermal energy storage, liquid metal turbines, bearings, and pumps. Although the design characteristics of dynamic space power systems are fairly well established, there are many materials problems whose answers will have great influence on the resultant system. Some of the questions are:

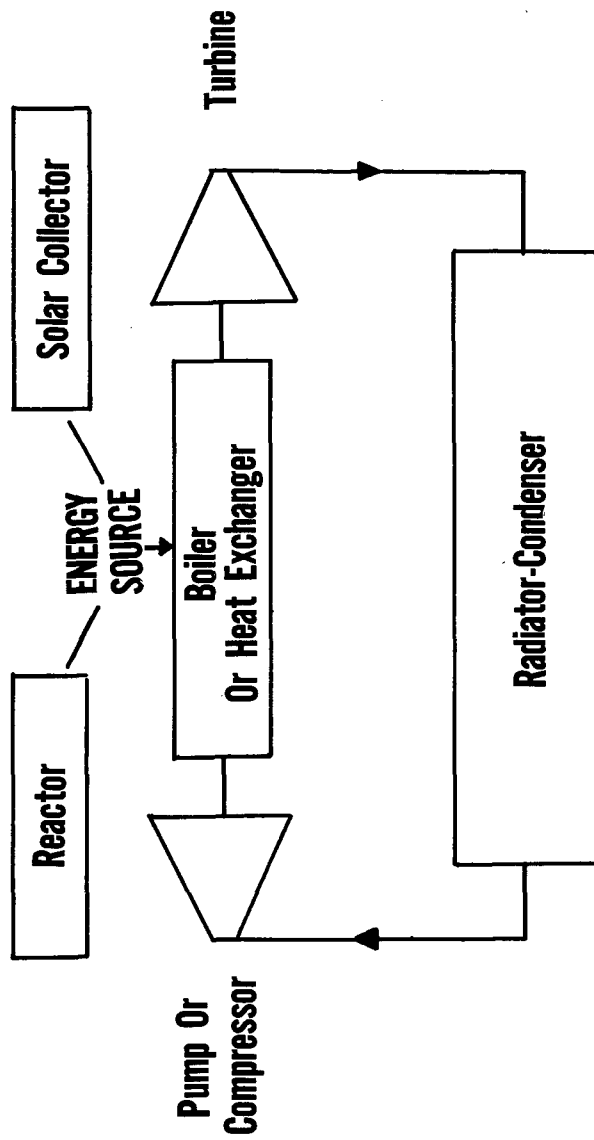
1. What are the temperature and velocity limitations with respect to corrosion, erosion, and mass transfer?
2. What are the thermodynamic properties of the fluids?
3. How serious is the sublimation rate of materials in a high vacuum?
4. Can foam materials be used in the construction of light weight and small volume collectors for required duration?
5. What are the contact resistances of materials? What roughness of the surface is required and what are the limits of contact pressure?
6. In bi-metallic systems (tube-fin, turbine-blade), what are the effects of differential expansion?
7. What are the best joining techniques in components of different mechanical and thermal properties?
8. How can a measurement standardization of surface coating be realized?
9. What are the temperature drop and bond strength of surface coatings?
10. What thickness of coating is required?
11. What are the mechanisms involved in meteoroid penetration?
12. What are the effects of various modes and frequencies on vibration characteristics of large exposed space areas?
13. How can we duplicate experimentally the effect of meteoroid penetration?

Thus we see that there is a continuing requirement for extensive materials experimental and applied research effort to make effective dynamic energy conversion systems possible.

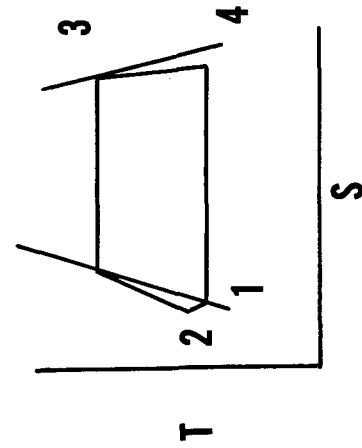
BIBLIOGRAPHY

1. Schipper, L., Weight Optimization of a Solar or Nuclear Mechanical Conversion System, WADC TN-59-180, June 1959.
2. Analysis and Development of a Space Heat Rejection System and its Optimum Integration into a Space Vehicle, Electro-Optical Systems, Inc., ABMA Contract DA-04-495-ORD-1473, December 1959.

DYNAMIC ENERGY CONVERSION SCHEMATIC



RANKINE CYCLE



BRAYTON CYCLE

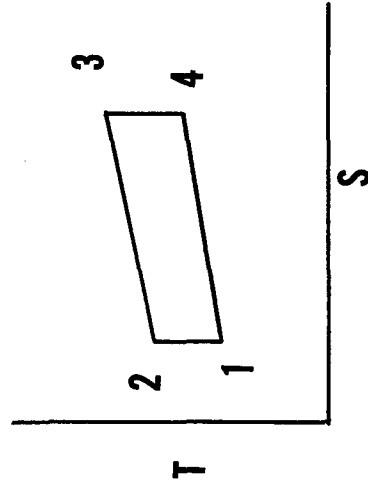


Figure 1.

SOLAR DYNAMIC SYSTEM

Orbit Time=100 Min
Shadow Time= 40 Min.

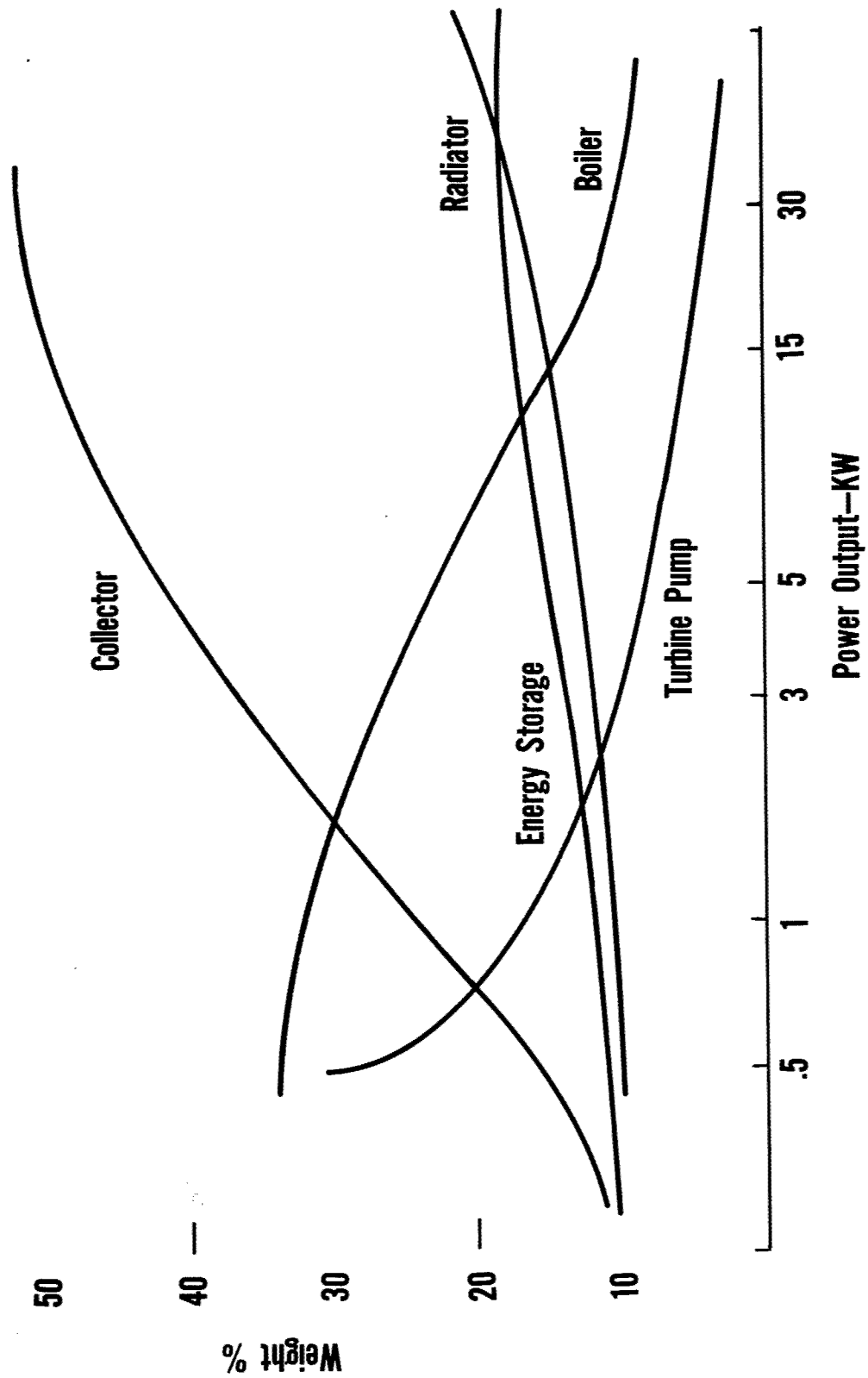


Figure 2.

COLLECTION EFFICIENCY

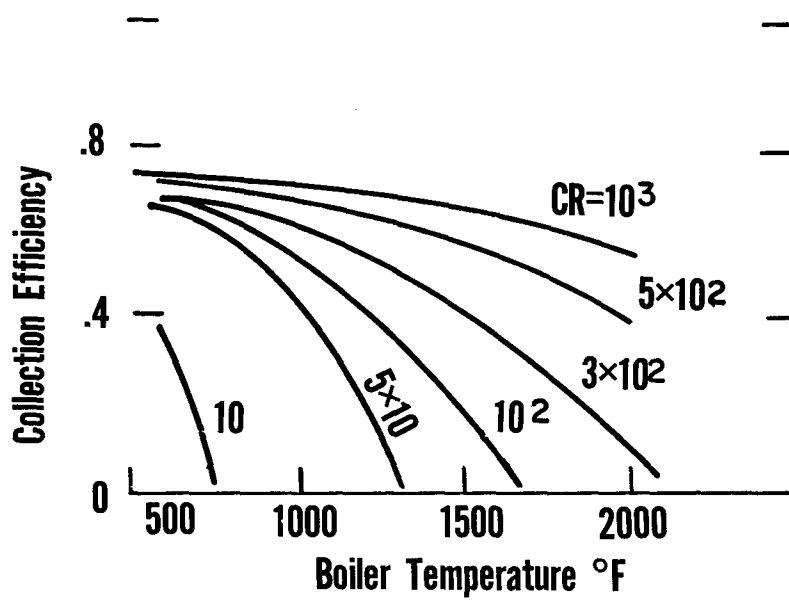


Figure 3.

NUCLEAR DYNAMIC SYSTEM

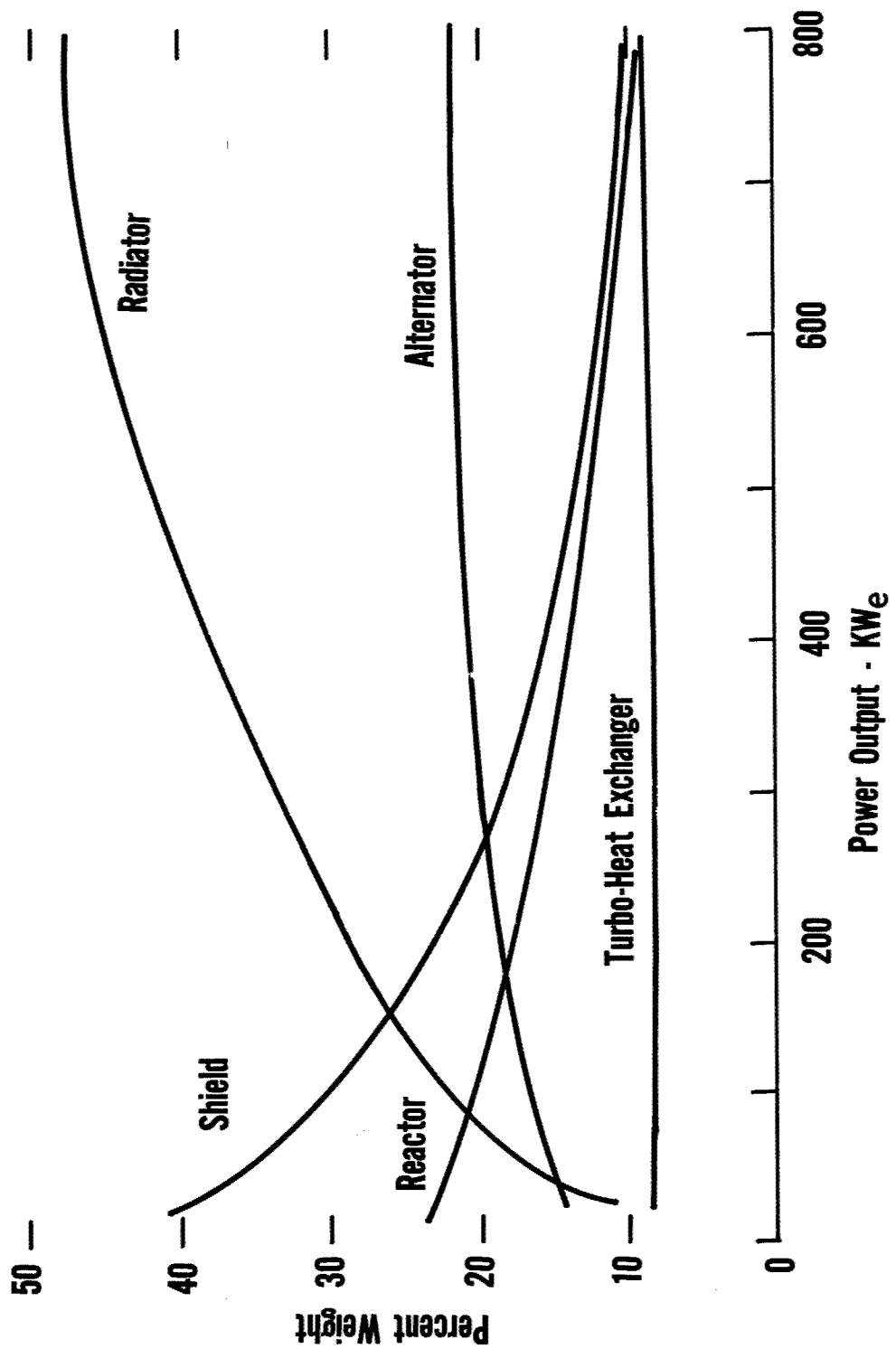


Figure 4.

EFFECTS OF INTERNAL HEAT TRANSFER

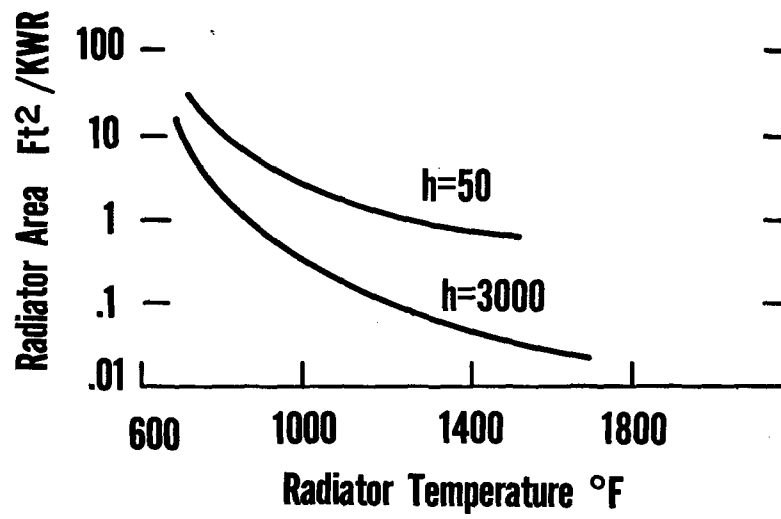


Figure 5.

OPERATIONAL AND EXTERNAL ENVIRONMENTAL CONSIDERATIONS

- **Meteoroids**
- **Radiation**
- **High Vacuum**
- **Reliability**
- **Weight And Volume**

Figure 6.

BELT RADIATOR

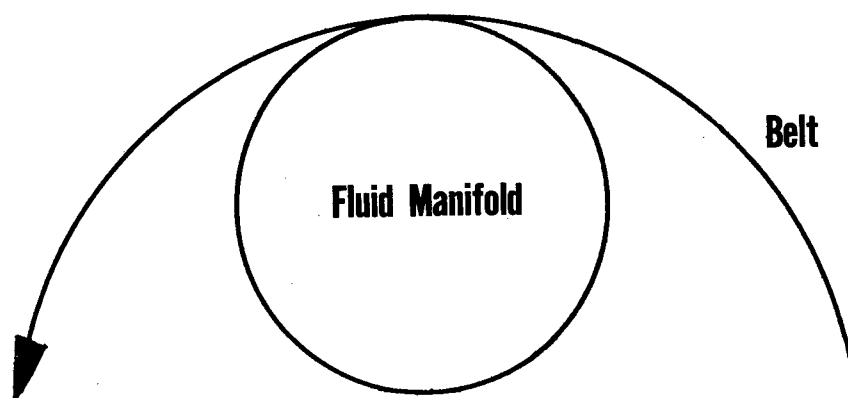


Figure 7.

TYPES OF THERMIONIC POWER CONVERTERS AND CURRENT MATERIALS LIMITATIONS

Capt. E. F. Redden

Directorate of Avionics, ASD

Thermionic power converters are static energy conversion devices that transform heat directly into electrical energy (figure 1). A thermionic generator consists of one or more of these thermionic converters coupled to give the desired power output. A thermionic generator has a number of distinct advantages over dynamic conversion devices. Some of these advantages are:

- a. Rotating equipment is not employed.
- b. Liquid-vapor phase problems do not exist.
- c. Separators for fluids are not required.
- d. Frictional losses due to bearings are not present.

Some of the disadvantages of thermionic generators are:

- a. Individual converters are low voltage, high current devices.
- b. A large number of converters must be sequentially arranged to obtain useful voltage.
- c. Power losses in leads and in the converters can seriously cut useful power output.

Thermionic generators can be operated from any primary heat source. For low power levels, i.e., three kilowatts or less, solar energy looks very promising. For higher power levels a nuclear heat source is required. In large nuclear thermionic generators of fifty kilowatts or more, a liquid-metal cooled reactor and pumping equipment will be required to dissipate waste heat to a radiator surface.

Thermionic power converters can be categorized for reference purposes in several different ways. We have chosen to classify thermionic converters according to the methods of neutralization space charge. On this basis the most frequently discussed are:

- a. Vacuum Close-Spaced and b. Cesium Gas Filled

Other breakdowns that emphasize the type of emitters employed are just as meaningful. In any case, electrons are emitted from a heated surface (cathode), move through an inter-electrode spacing, and are collected on an anode. Electrons are returned to the cathode through an external load.

Three important aspects must be immediately considered in all thermionic converters:

- a. The cathode must emit an abundant supply of electrons.
- b. Evaporation of atoms from the cathode surface should be negligible.
- c. Electronic space charge build-up in the inter-electrode spacing must be eliminated.

Search for solutions to these problems account for the number of programs being investigated on thermionic power converter technology.

The cathodes of thermionic converters must be operated in excess of 1100°C to obtain a satisfactory current density from the emitter surface. In addition, the emitter must be compatible with the cesium environment around it and have a low evaporation rate. Emitter materials currently being investigated are (see figure 2):

- a. Simple metals (molybdenum and tantalum)
- b. Tungsten impregnated with barium oxide
- c. Solid solutions of mixed carbides (uranium carbide-zirconium carbide)

The physical and chemical properties of the basic metals are fairly well defined. The investigations on the more complex emitter materials have been based on trial and error experiments. A systematic search for high electron emission compounds should be continued.

The vacuum close-spaced converter which has been under extensive investigation since 1957 was the first attempt to solve the electronic space charge problem. This type of converter looked promising provided a physical spacing of 0.0005 inch or less could be maintained between the cathode and anode. This has been a difficult engineering feat because temperatures on the cathode surface were 1100°C . In addition, there were other problems that arose:

- a. Relatively high barium evaporation rates from the cathode
- b. Deposition of barium on cathode-anode spacers
- c. Different expansion rates for impregnated tungsten and tungsten
- d. Warpage of cathode followed by shorting of converter
- e. Pulverization of cathode-anode spacers
- f. Inability to remove copper from the emitter (Copper is initially added to improve cathode machineability)

The vacuum converters average approximately 3 percent efficiency and a lifetime of 40 hours.

Use of positive ions in the inter-electrode spacing of thermionic converters permits a wider separation between the cathode and anode. If thermionic converters are to be mass produced, this is an important consideration (figure 3). Almost any positive ion will suffice to neutralize electronic space charge provided materials compatibility is satisfied. Ideally, an inert gas or mixtures of inert gases should be used; however, cesium is usually employed because of its proneness to ionization. In experimental thermionic converters cesium is admitted from a temperature controlled well. Experimental thermionic converters regulate cesium pressure in the inter-electrode spacing. In thermionic converters with high work function cathodes and when operated at high temperature, most of the cesium ionization occurs by contact ionization with the cathode surface. In lower temperature cesium filled converters and in those that employ low work function cathodes, much of the ionization occurs by collision processes. The operation of thermionic converters at high temperature and the introduction of a corrosive alkali metal adds a completely new problem to thermionic power converters (figure 4). All

converter components, anode, cathode, seals and envelope must be resistant to cesium corrosion. To date, one of the major problems has been in seals. In fact, most cesium filled thermionic converter failures can be blamed on corrosive destruction of seals by cesium.

So far as known, cesium filled power converters have never been operated in excess of 600 hours. Failures to date can largely be blamed on seal failures and loss of cesium in the inter-electrode spacing. Efficiencies are tricky to quote and often misleading unless lifetime is also quoted; however, 15 - 17 percent is not uncommon.

In the lower power ranges of 3 kilowatts or less, thermionic converters may find application in solar generators. In the higher power levels up to megawatts, thermionic converters appear very promising for use with nuclear reactors. Converters may be operated as an intimate part of the nuclear reactor or exterior to the reactor. The radiator of a liquid metal cooled reactor is a good location for thermionic converters. The converters can extract heat from the liquid metal plus serve as a very good protection to vulnerable liquid metal tubing. Thermionic generators are three to five years away from initial application in aerospace vehicles although experimental test flights could be undertaken in approximately two years. Low power solar heated generators look most feasible within this time period. To attain the goal of thermionic converter application in aerospace vehicles within the three to five year period, extensive research is required on:

- a. High temperature seals
- b. Low evaporation rate emitters

A better understanding of the high temperature chemistry of cesium in the environment of the individual thermionic converters is mandatory. Coincident with the cesium investigation, search for low evaporation rate materials should continue and fundamental investigations to improve life expectancy of existing cathode materials should be made.

PLASMA CELL DIODE

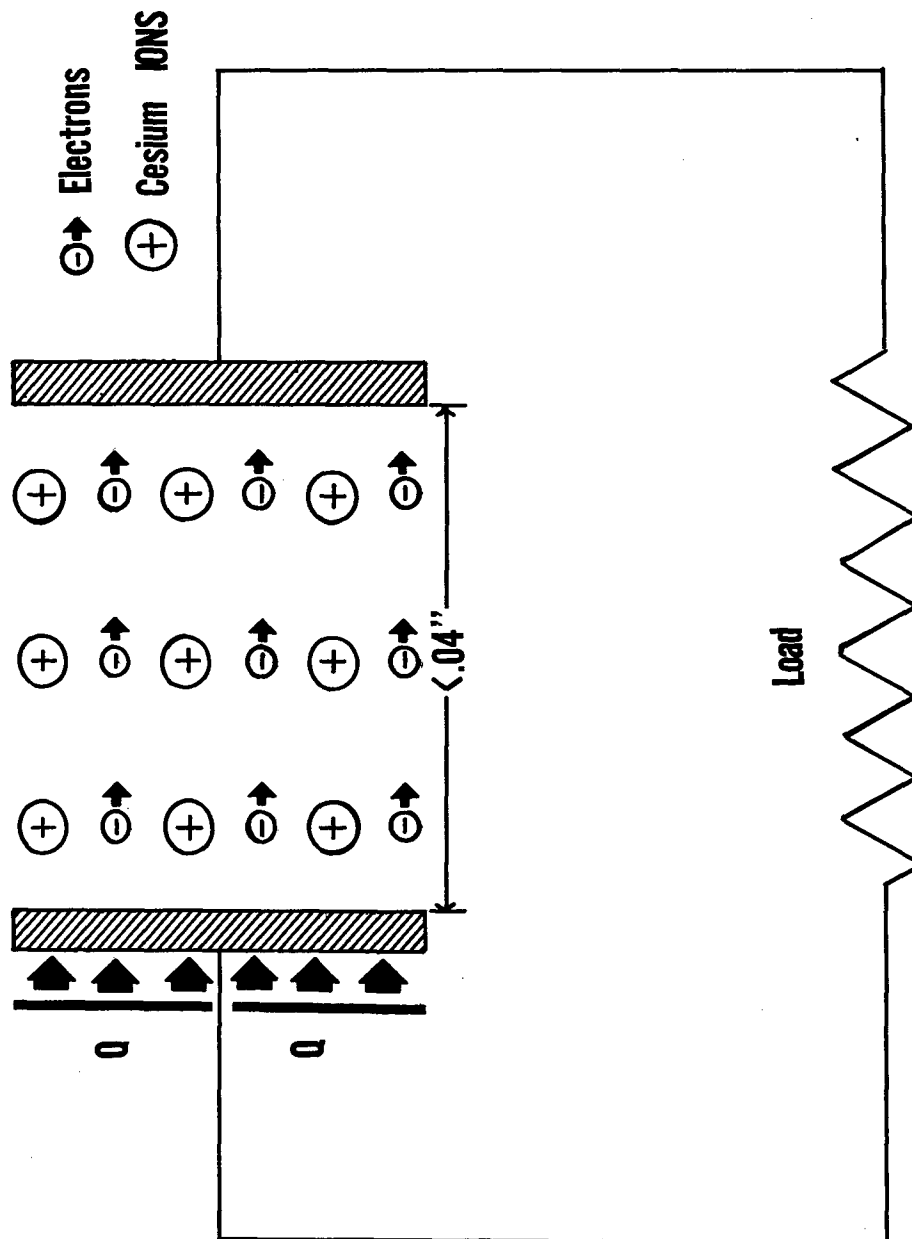


Figure 1.

EMITTER MATERIALS

EXTENSIVE RESEARCH		LIMITED RESEARCH
Simple Metals	W	Re
	Mo	La B 6
	Ta	Borides, Nitrides, Carbides
Oxides	Ba	
	Sr	
	Ca	
Carbides	U-Zr	

Figure 2.

SPACE CHARGE NEUTRALIZATION

EXTERNAL RESEARCH

LIMITED RESEARCH

Vacuum

Neon-Argon

Cesium

Fission Fragments

Rubidium

Figure 3.

INSULATOR WELDS BRAZES

Al_2O_3	ELECTRON BEAM	Cu^{**} , Ag^{**} , Au
BeO	Cu-Mo	Binders (Zr)
HfO_2	Ta-Cu	Ta-UC-ZrC
	Cu-Steel	
	Cu-Fe/Ni Alloys	

* Electron Beam Used To Prevent Poisoning Of Converters

** Ag, Au Attacked By Cs - Mg

Figure 4.

SOLAR CELLS IN SPACE

Russell W. Rummels

Electronic Technology Laboratory, ASD

Devices and Materials

The increasing use of the photovoltaic solar cell as an energy conversion device for the utilization of solar energy, providing the electrical power for the orbital satellite, has resulted in several programs for improving the state of the art. Obviously, this solar energy being converted is provided for our use at the lowest imaginable price — free! Since this is the case, it becomes essential that means be developed for the greatest possible employment of this power. Hence, there has been considerable emphasis placed on the investigation of photovoltaic device improvement.

There are many avenues of approach that one can take to achieve the objective of increasing device capability for utilizing the solar spectrum. Even though there are several approaches, there are only two facets of the photovoltaic cell that can be investigated. They are device design and material exploitation. Neither of the facets are simple matters.

The Electronic Technology Laboratory designed a program for the advancement in the state of the art of solar cells and interesting results were obtained. The following paragraphs will explain the seven areas investigated.

At the initiation of the original program (1959), the most obvious investigation was to improve the much used silicon cell. One of the objectives of the program was to achieve a 15 percent conversion efficiency in the "standard" 1 x 2 cm unit. Having accomplished this objective, the program continued the research on dendritic materials. In this research a 15 percent conversion efficiency was to be maintained, but, only 13.5 percent conversion efficiency was produced. Concurrent with exploiting dendritic materials, the formation of epitaxial layers of material was investigated. Epitaxial cells are behind the state of the art of the "standard" 1 x 2 cm unit and the dendritic cells. The highest efficiency reported in the epitaxial cells was 8+percent.

The next item to be considered in device improvement is the material employed as the active element of photovoltaic cells. A survey was made of the various materials and the technology associated with each material was considered. Loferski, et al, showed that the "ideal" material for solar energy conversion would have a band gap greater than that of silicon, but would probably be close to 1.6 ev. However, very few materials satisfy this criteria, therefore, one must seek a material which would approach this value and still show promise of surpassing silicon cell capability. It would also be necessary that the basic material parameters, such as resistivity, mobility, carrier concentration, band gap, and similar properties must be known to a reasonable degree of accuracy to form a firm foundation for material selection. With these considerations in mind, the material offering the greatest potential was gallium arsenide (GaAs). The Electronic Technology Laboratory sponsoring a large effort in GaAs, found that the material technology was in an excellent state of perfection. Having a band gap greater than that of silicon, higher operational temperatures are to be expected. Figure 1 identifies the rate of degradation of both silicon and GaAs cells as a function of temperature. These rates of degradation were established as a result of the experiment.

In order that advancement in device capability could be made, the same parameters governing improvements in silicon cells would require investigation in GaAs. At the initiation of the program, GaAs cells were 5 to 6 percent efficient. As one reviews the progress of the program, it becomes apparent that a steady, month-by-month improvement was obtained, although material parameters are considerably more stringent in GaAs than they are in silicon and excellent results were reported. Not only was the objective nearly reached, but reproducibility between units was obtained. The program objective was set at achieving a 15 percent conversion efficiency. The highest value reported thus far was 14.7 percent. However, since gallium arsenide cells are in very short supply, the use of silicon cells must be continued to fulfill the quantity requirements.

Since many ideas have evolved whereby a greater utilization could be made of the solar spectrum through unusual device design, it was necessary that such structures be exploited for a determination of their capabilities as energy converters. Composite cells, stacked cells, variable band gap units, and polycrystalline films were among the unique units investigated. The result showed that although very definite gains could be made in greater spectrum utilization, the cost was too high and the project somewhat impractical to continue. The polycrystalline structure does hold promise for obtaining very large areas at reasonably low cost. The material presently being studied under this portion of the overall program is Cadmium-Telluride (CdTe). However, there has not been sufficient time or effort expended on the material to form any sound conclusions as to the capability of the material as a polycrystalline photovoltaic cell.

Now that we are attempting to maximize utilization of the solar spectrum outside the atmosphere, one seeks the answer to the question of: What is the best material for cell use? This is another part of the Electronic Technology Laboratory's program. The objective of this part of the program is to search for an "ideal" material to utilize the spectrum from 0.2 to 2.0 micron wavelength. Following a comprehensive literature survey, it was decided to study aluminum antimonide (AlSb) as the photovoltaic material. Obviously AlSb is not the "ideal" material, since it does not respond to the longer wavelengths of the spectrum, therefore other materials are being considered from a theoretical standpoint. Certain ternary compounds are presently being considered.

Device Capability

To determine the actual solar cell capability when operating under space conditions, it is necessary that the evaluation of cells be accomplished by either placing them aboard a satellite and receiving telemetered data concerning their operation, or within a simulated environment, or both. Unfortunately, space aboard various orbital vehicles is at a premium and therefore the evaluation is usually done with simulation techniques. However, simulation of the solar spectrum is not done easily. The light sources employed for evaluation range are color, temperature controlled tungsten bulbs to photoflood bulbs, and high pressure arc systems. Water filters are used to reduce the IR content of sources; liquid and gelatin filters are used to obtain a close approximation to a blackbody radiator; and multiple light sources are used to "fill in the gaps" in a given desired spectral distribution.

Evaluation techniques are nearly as varied as are the light sources. Black boxes are used to cut down reflections, monochrometers are used to determine light source spectral characteristics, thermopiles and pyrheliometers are used for intensity checks, and often the sunlight is employed for measurement correlation depending upon time of day, year, humidity conditions, and geographic location.

Under these conditions, it becomes very difficult for an applications engineer to design a solar cell panel having a particular set of characteristics, because the data on cell operation which is supplied to the designer leads to considerable confusion. If gallium arsenide, cadmium sulfide or some other compound semiconductor is employed in the cells to be used, then the design engineer has an entirely different set of conditions to work with, in comparison to silicon cells; the reason is simply that no two materials have the same spectral response, therefore do not respond to the same light source in the same manner. The only true method of determining cell operation would be to employ a sun simulator having the same spectrum as the sun.

Now let us combine the whole problem by adding temperature control problems, plus radiation and micrometeorite damage!

To better evaluate cells, and to stir the general thinking of all concerned with devices and their operation, the Electronic Technology Laboratory had a solar simulator designed and built, with emphasis on the light source. The simulator was intended to reproduce the solar spectrum from 0.2 to 2.0 microns or as near as possible. Not only must the solar spectrum be reproduced, but the intensity should fluctuate from a fairly low value, to well above that of space near the earth. Further, the system would employ a cooled vacuum chamber to determine cell operation under specific vacuum and thermal conditions. The simulator shown in figure 2 has been installed at the Electronic Technology Laboratory.

The light source employed is a plasma jet ionizing argon gas. The source simulates the spectrum as defined by Stair and Johnston to a fairly good approximation. Figure 3 depicts the spectral distribution taken of the sun under "one sun" intensity. One sun intensity is defined as 143.0 mw/cm^2 as found outside the atmosphere. The spectrum, as noted in figure 3, has been determined from 0.2 to 0.7 microns. The remainder of the spectrum from 0.7 to 2.0 microns is yet to be determined.

Using the solar simulator at ETL, the devices resulting from all of the applied research efforts, manufacturing methods programs, and cells supplied from commercial organizations were subjected to evaluation. It was found that the electrical characteristics of nearly all silicon units were somewhat optimistically stated by each supplier. Reproducibility between units of the same manufacturer also left something to be desired. Silicon units from commercial suppliers are generally 1 to 2 percent lower in efficiency than identified in data sheets. The evaluation of silicon dendritic cells manufactured by Westinghouse and evaluated in the ETL simulator often show good correlation between data taken at Westinghouse and ETL. Identical values have been obtained, but data are generally about 0.5 to 1.0 percent lower when taken with the ETL simulator.

The data on GaAs cells as evaluated at RCA and at ETL show the greatest degree of correlation and are generally within 0.5 percent of each other. Unfortunately, quantities of gallium arsenide cells are not available at this time, and until this problem is alleviated, system demands will have to be supplied from silicon units.

According to the most recent published data sheets, the value of solar intensity to which cells are being supplied by the various manufacturers is in accord with the value that has been determined to exist outside the earth's atmosphere. The solar spectrum is specified in most instances to a close approximation of that found outside the atmosphere. With cells supplied by these two factors the design engineer can more realistically establish a panel construction without over-design.

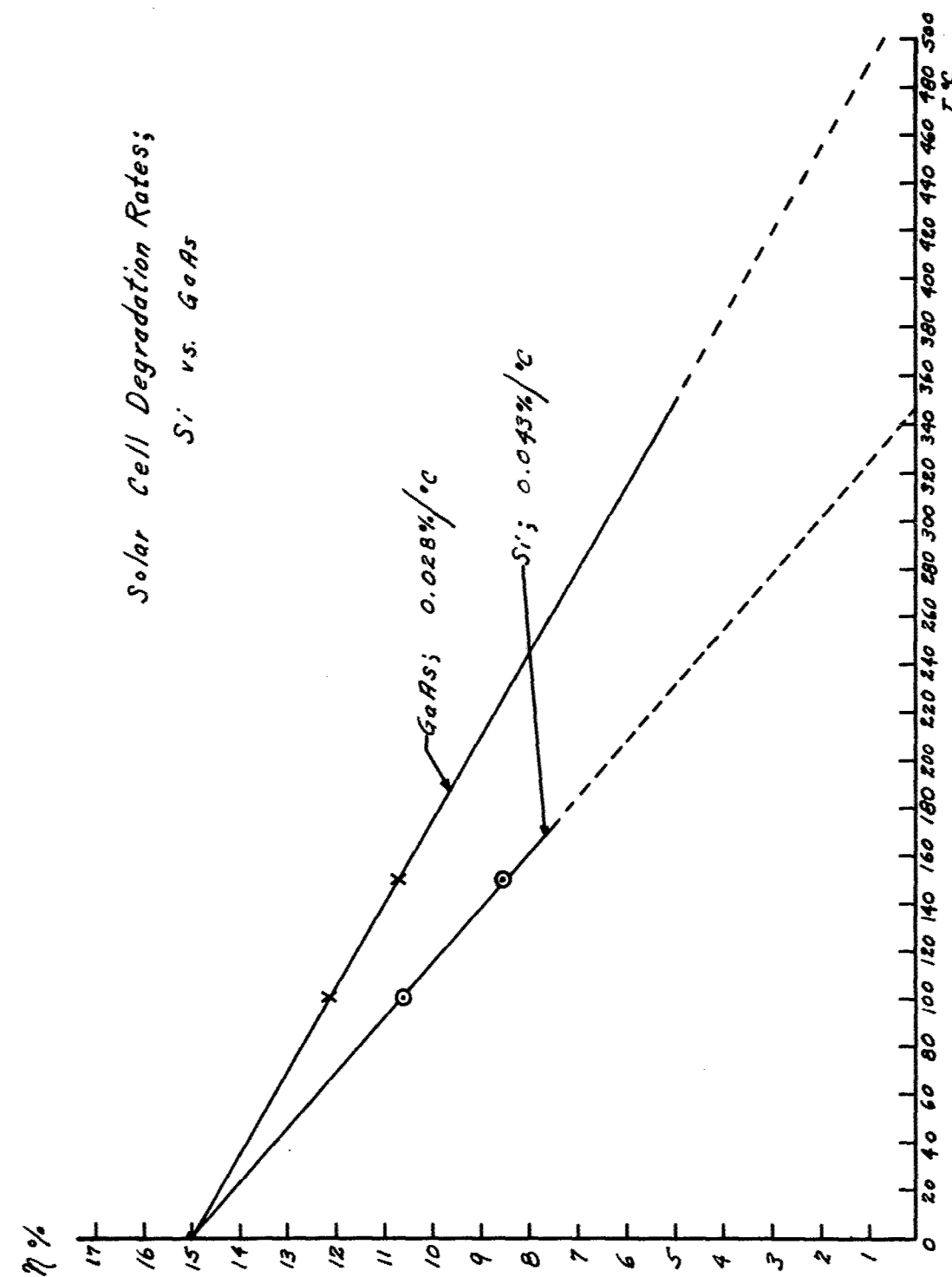


Figure 1.

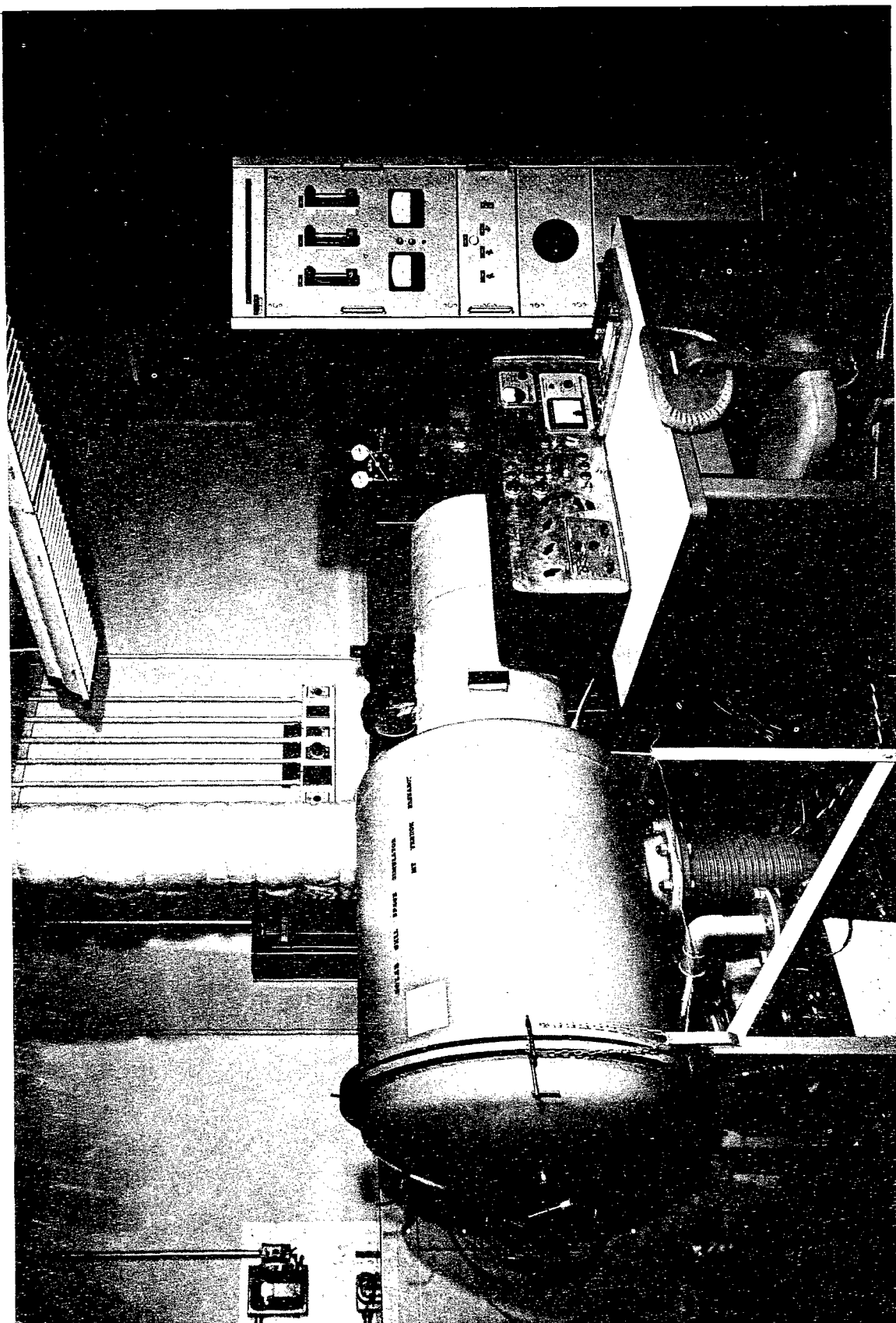


Figure 2.

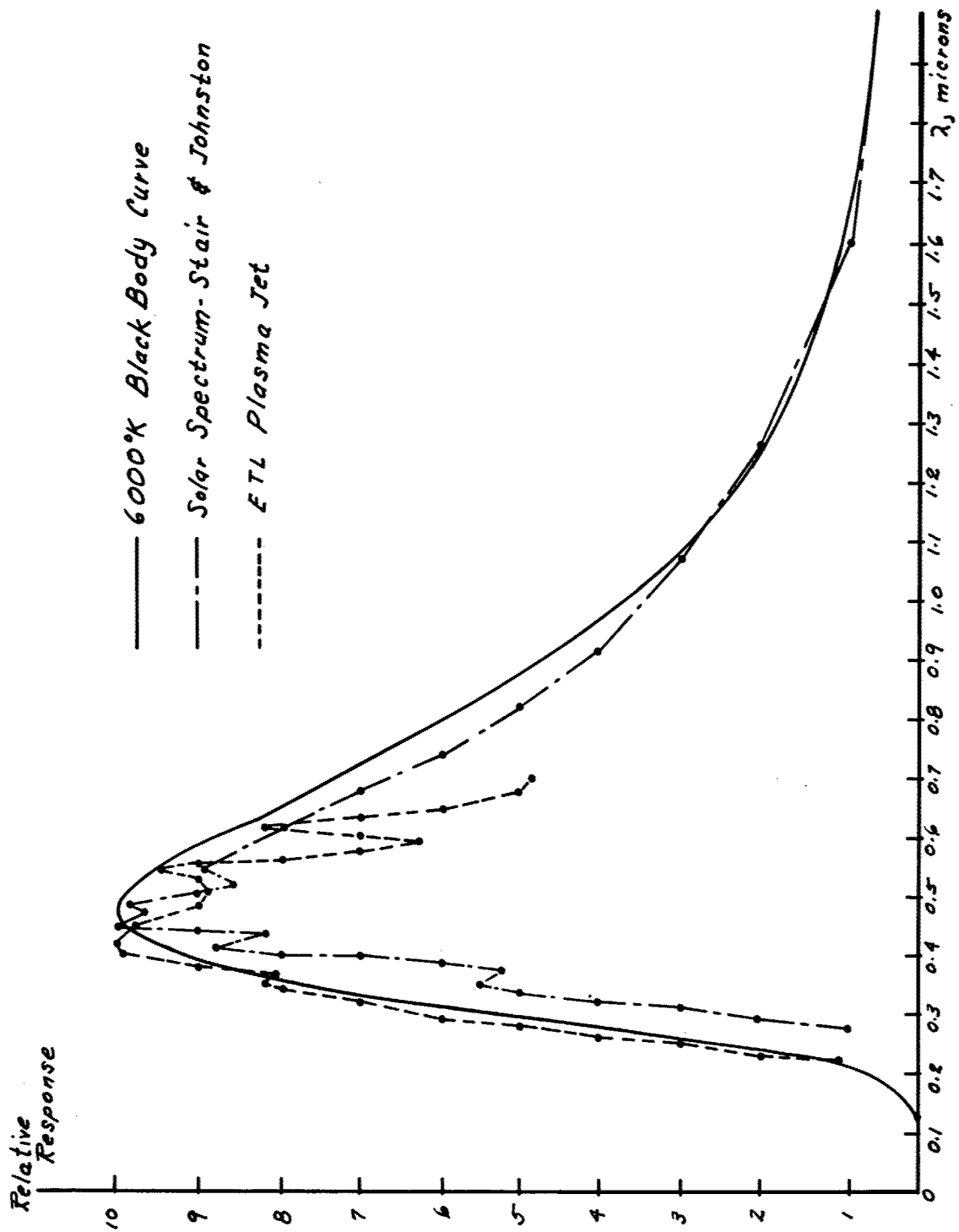


Figure 3.

MATERIALS FOR ENERGY CONVERSION SYSTEMS

B. Rubin

Directorate of Materials and Processes, ASD

Space flight with its tremendous extension of attainable altitude, observable areas, and communication capabilities within compressed time periods promises to provide the ability for important changes in our civilization. Unmanned exploration was initiated with Sputnik and the some 30 satellites which followed. Manned travel in cislunar space has recently become a demonstrated capability. Both the Soviet Union and the U.S. have launched unmanned Sun and solar planetary probes. By the mid-1960's we expect to move from exploration to utilization of the space environment for purposes such as navigation, mapping, weather observation, reconnaissance, communication and air traffic command and control with both unmanned and manned vehicles.

In all the above applications, power is required to accomplish any intended task or combination of tasks. The power will most probably be electrical and must be reliable over long time periods, light weight, reasonably efficient, and economical. The energy conversion process, by various techniques, converts a relatively narrow band of the energy spectrum into useful energy for power.

However, regardless of the conversion cycle being considered by the aerospace engineer, whether it be: thermoelectric, thermionic, fuel cell, solar cell, photovoltaic, mechanical-dynamic, magneto gas plasma-dynamic, the materials used, determine the ultimate feasibility, efficiency, longevity and reliability.

The materials research and development efforts of several scientific and engineering disciplines provide direct capability and impetus to developments in energy conversion processes and systems. The nature of the Directorate of Materials and Processes research and the state of the art in some pertinent areas will be discussed. Our effort has been concentrated on synthesizing and developing into useful form, materials with potential for broad usage, and in the characterization of the mechanical, thermal, optical, and electrical properties over wide temperature ranges of environment. Studies in refractory metal alloys, ceramics, graphite, surface coatings, high polymers, and techniques for measuring thermophysical properties of solids and fluids are of particular interest.

Let us examine some of the facets of applied research as they bear directly on the energy conversion process.

The temperature levels of materials for the mechanical aspects of dynamic systems indicate a range of requirements from modest levels (500° - 800°F) to temperatures in excess of 2000°F with the higher temperature relating to high power output at low weight-to-power ratios. Materials can be chosen from limiting thermal and dynamic stress data. Design fluid containment, rotating parts, and some materials for the gamut of temperatures are shown in figure 1. However, the strength-weight-temperature curve lacks an important ingredient - the time factor. The long life requirements dictated a necessity for reliable data at 10,000 hours. Figures 2 and 3 show estimates of the strength-weight ratio and creep to yield ratio for the 10,000 hour period. These estimates, especially at the higher temperatures (above 1000°F), are based on meager amounts of stress-rupture and creep data and at times up to 1000 hours, with up to 100-300 hours

at 2000°F. Obviously, an increase in the amount and duration of time data would greatly increase confidence in use of the high temperature materials and insure a more reliable design of minimum weight.

The transfer of thermal energy and its conversion to mechanical power are accomplished by heat transfer and working fluids. These two functions may require different, or the same fluids with the latter preferable where feasible. The vapor pressure chart (figure 4) shows fluids which are being used and being considered for use. The significant fact is that internal pressure and stability considerations have led to the use of metallic materials which are liquid in the -40° to 400°F range. Extensive effort is being devoted to characterization and critical review of the physical and thermodynamic properties in the liquid and vapor state of these materials and certain elements and salts.

The use of these materials, however, produce containment problems—compatibility with tubing and system components. The compatibility of materials and working fluids is one of the more serious problems requiring careful and diligent attention. Compatibility problems may be divided into three major categories—corrosive attack, erosion, and fouling. The chart (figure 5) describes the relationship.

The rate of corrosive attack on metal surfaces by non-aqueous inorganic liquids may vary significantly with flow rate if the slowest step in the corrosion process is the rate at which the solute diffuses through the liquid boundary layer. On the other hand, the corrosion rate may be independent of the flow rate if the slow step is the rate of dissolution of the solid or the rate of diffusion of the solid phase. Iron-mercury typify the first of these cases and iron-sodium and iron-molten salt are representatives of the latter.

In certain instances, the net thermal gradient mass transfer of pure metal phase from a hot zone to a cold zone may proceed by way of formation of an intermediate compound. For example, sodium oxide dissolved in liquid sodium may react with iron in a hot zone to form an iron-sodium-oxygen compound. This compound may revert to sodium oxide and iron in a cool zone and thereby cause a net transport of iron, resulting in intergranular corrosion and blockage of tubes and orifices.

In the case of the liquid alkali metals, the presence of dissolved oxygen or oxide (and dissolved nitrogen or nitrides in the case of lithium) increases fluid corrosion activity. This enhancement of corrosion activity may result from compound formation as noted above, or it may reflect the surface fluxing ability of dissolved oxide. The problem may be minimized by starting with an initially clean fluid in a clean system, or by cold trapping oxide contaminants as solid oxides.

Static compatibility data are shown in figure 6 for rubidium and lithium. The usefulness of the refractory metal alloys is apparent and the compatibility problems of joined areas in contact with the liquid metal environment are obvious.

Collection and efficient utilization of absorbed energy and rejection of unused heat to a heat sink are important design considerations of many energy conversion systems. The surface properties of materials are important facets of both energy absorption and rejection. Solar radiation offers a virtually inexhaustible source of energy, and all space flights, except very short ones, to date have been powered by the direct photovoltaic quantum conversion of solar energy using silicon solar cells. The newer systems under study, e.g. thermoelectric, thermionic, and turbine drives, are dependent upon the thermodynamic conversion of energy from a source heated by solar irradiance or nuclear energy. Fundamental to these systems is an energy receiver having high absorption in the spectral

range from $0.3\ \mu$ to $2.0\ \mu$ (which include about 94 percent of the solar energy) and having low radiation loss over the range of operating temperatures. This combination of requirements are direct functions of the receiver surface optical properties. To achieve high thermodynamic efficiency in a power system, a large temperature differential between heat input and heat rejected is required.

High absorption of solar energy is readily obtained. However, reradiation of this energy, and this becomes significant at high temperatures, becomes the chief loss of power. There are several approaches to overcoming the reradiation problem and achieving the desired balance of surface optical properties -- namely, high solar energy absorption with low emittance. The Directorate of Material and Processes is exploring the use of "interference" coatings to obtain selective energy absorption on the so-called dark mirror concept. To get selective energy absorption, the coating system must have high absorption for short wavelength light and high reflection (low emittance) for long wave length light. The coating consists of extremely thin films of metals deposited alternately with a dielectric film. About 90 percent absorption can be obtained in a three-layer film. Figures 7 and 8 show the percent of solar energy absorbed and percent reradiated of a silicon monoxide-aluminum-silicon monoxide coating on an aluminum substrate at 600°K . The high degree of energy absorption and low energy loss by reradiation show the efficiency of this system. Development of stable coating systems, chemically inert, non-volatile, and with low diffusion into substrates at high temperatures are required.

What of the other side of the coin? Systems using fluid heat transfer must eventually reject heat by radiation to the infinite sink of space through a radiator. For a given temperature, the amount of heat radiated is directly proportional to the emissivity. The desired characteristic is high emissivity at as high a temperature level as is compatible with the system design and the radiator material. The total normal emissivity of some of the oxidized metallic surfaces can be enhanced by the application of coatings. A recent design study indicated that a condenser radiator made of Hastelloy tubing and beryllium fins and operating at a fluid temperature of 1500°F would be 30 percent lighter with an emissivity $E = 0.9$ as compared to an $E = 0.5$. Directorate of Materials and Processes has obtained emissivity data on a great many materials. Coatings which enhance emissivity often have been a by-product of other research rather than a direct effort in this area. Coatings for refractory metal alloy oxidation protection are an example. The emissivity of these special coatings and oxides after long use at high temperatures and under high vacuum is an unknown and uncertain quantity.

Since the most desirable choice of materials for a given conversion application is often highly dependent upon subtle variation in properties, great emphasis has been placed on developing suitable techniques for measuring these properties over wider ranges of temperature. Measurement techniques for extreme conditions continue to be studied and much useful data continue to accumulate. However, only recently has there been a concerted effort to obtain, collate, critically review, and catalog these data. Several reports have been issued recently containing physical properties on a great variety of solid, liquid, and gaseous materials. The properties include density, thermal conductivity, heat capacity, thermal expansion, vapor pressure, heat of sublimation, electrical conductivity, Seebeck coefficient, emissivity, and transmittance. Such data, when readily available, greatly assist in firming up the heat transfer, optical, and electrical characteristics that might be expected of a system components. Plots typical of this data are shown in figures 9, 10, 11, 12, 13 and 14.

Some interesting considerations appear from such compilations. At about 2000°F, we have reached a limit in the usefulness of known magnetic materials. We can add the time ingredient to vapor pressure data by application of theoretical considerations and arrive at estimates of the loss of materials at temperature and in a vacuum — an important consideration in thermionic devices which employ high temperature cathodes. Tables 1 and 2 illustrate this point.

In summary, we have indicated through specific example where current research in several materials disciplines is providing direct and indirect support to various facets of the energy conversion process. Areas which require continued research emphasis and new research have also been indicated.

BIBLIOGRAPHY

1. WADD TR 60-773 "Coatings for the Aerospace Environment," R. Van Vliet, 9-10 Nov 1960.
2. WADD TR 59-598 "Properties of Inorganic Working Fluids and Coolants for Space Applications," W.D. Weatherford, J.C. Tyler, and P.M. Ku, Dec 1959.
3. WADD TR 60-523 "Applicability of Present Creep Prediction Techniques for Extrapolating Very Long Time Creep Behavior," K.D. Shimmin, Oct 1960.
4. DMIC Memorandum 103 "The Emittance of Coated Materials Suitable for Elevated Temperature Use," Battelle Memorial Institute, 4 May 1961.
5. "Nuclear Turbogenerators for Space Flight Vehicles," American Society for Metals Conference on "Space Age Metals," Cincinnati, Ohio, April 1960.
6. WADC TR 58-476 (AD 207905); "Thermophysical Properties of Solid Materials," (Broad Critical Survey of Thermophysical Literature) Armour Research Foundation, January 1959.
7. WADD TR 60-56 (OTS PB 161093); "Thermophysical Properties of Cryogenic Materials," NBS Cryogenic Engineering Laboratory.
8. WADD TR 60-581 "Thermal Properties of Refractory Materials," Atomics International (NAA).
9. WADC TR 57-487 (AD 150954); "Thermal Properties of High Temperature Materials," Armour Research Foundation, Feb. 1958.

BIBLIOGRAPHY (Cont'd)

10. WADC TR 56-222 "Determination of Emissivity and Reflectivity Data of Aircraft Structural Materials on Aircraft," Part I. (AD110458) "Techniques for Measurement of Total Normal Emissivity and Reflectivity with some Data on Copper and Nickel," October 1956. Part II. (AD202493) "Techniques for Measurement of Total Normal Emissivity, Normal Spectral Emissivity, Solar Absorptivity, and Presentation of Results," October 1958. Supplement I. (AD202494) October 1958. Part III. April 1960.
11. WADC TR 59-346 "Plasma Jet Temperature Study," General Electric Co., Feb. 1960.
12. WADD TR 60-102 "Investigation of High Emittance Coatings to Extend the Mach Number Range of Application of Structural Materials," Republic Aviation Corporation.
13. WADD TR 60-370 "Thermal Radiation Properties of Materials," University of California.
14. WADC TR 59-300
Part I "Research and Development Services Leading to the Control of Electrical Properties of Materials for High Temperature Radomes," Armour Research Foundation, October 1959.
15. WADC TR 59-337
Parts I and II "Synthesis and Purification of Dielectric Materials," Westinghouse Electric Corporation, Part I, Oct. 1959; Part II, Sept. 1960.
16. WADC TR 58-13
Parts I, II and III "High Temperature Insulation for Wire," Georgia Institute of Technology; Part I, March 1958; Part II, July 1959; Part III, March 1960.
17. WADC TR 59-303 "Methods of Purification of Metals and Intermetallic Compounds," Armour Research Foundation, November 1959.
18. WADD TR 60-111 "Organic Semiconductor Study," Hughes Research.
19. WADC TR 58-535 "Long Term Magnetic Stability of Alnico V and Other Permanent Magnet Materials," Indiana Steel Products Co., Dec. 1958.
20. WADD TR 60-421 "Investigation of the Stoichiometric and Structural Variables Which Affect Conductivity in Ferro-magnetic Ceramic Materials," General Electric Corp.

TABLE 1 LOSS OF POTENTIAL CATHODE MATERIALS BY VAPORIZATION		
MATERIAL	T_{\min} - °K	VAPORIZATION RATE AT T_{\min} - cm/yr
TANTALUM	3010°	13
TUNGSTEN	3310°	54
RHENIUM	3630°	1.97×10^3
NIOBIUM	2910°	92
MOLYBDENUM	3100°	2.94×10^3
URANIUM CARBIDE	2330°	2
T_{\min} - MINIMUM TEMPERATURE REQUIRED FOR EFFICIENT CATHODE OPERATION		

TABLE 2 EVAPORATION OF METALS AND SEMICONDUCTORS IN HIGH VACUUM				
ELEMENT	TEMPERATURE (°F) AT WHICH EVAPORATION IS			MELTING POINT °F
	10^{-5} cm/yr	10^{-3} cm/yr	10^{-1} /cm yr	
Se	120	180	240	430
Te	260	350	430	840
Mg	260	350	460	1200
Li	300	410	530	370
Al	1020	1260	1490	1220
Be	1140	1300	1540	2340
Cu	1160	1400	1650	1980
Si	1450	1690	1970	2580
Pd	1490	1720	2020	2840
Ti	1690	1960	2280	3140
Pt	2120	2440	2840	3240
Zr	2340	2740	3150	3360
Mo	2520	2960	3450	4700
C	2780	3050	3400	6600
Ta	3250	3700	4200	5400
Re	3300	3700	4200	5700
W	3400	3900	4500	6100

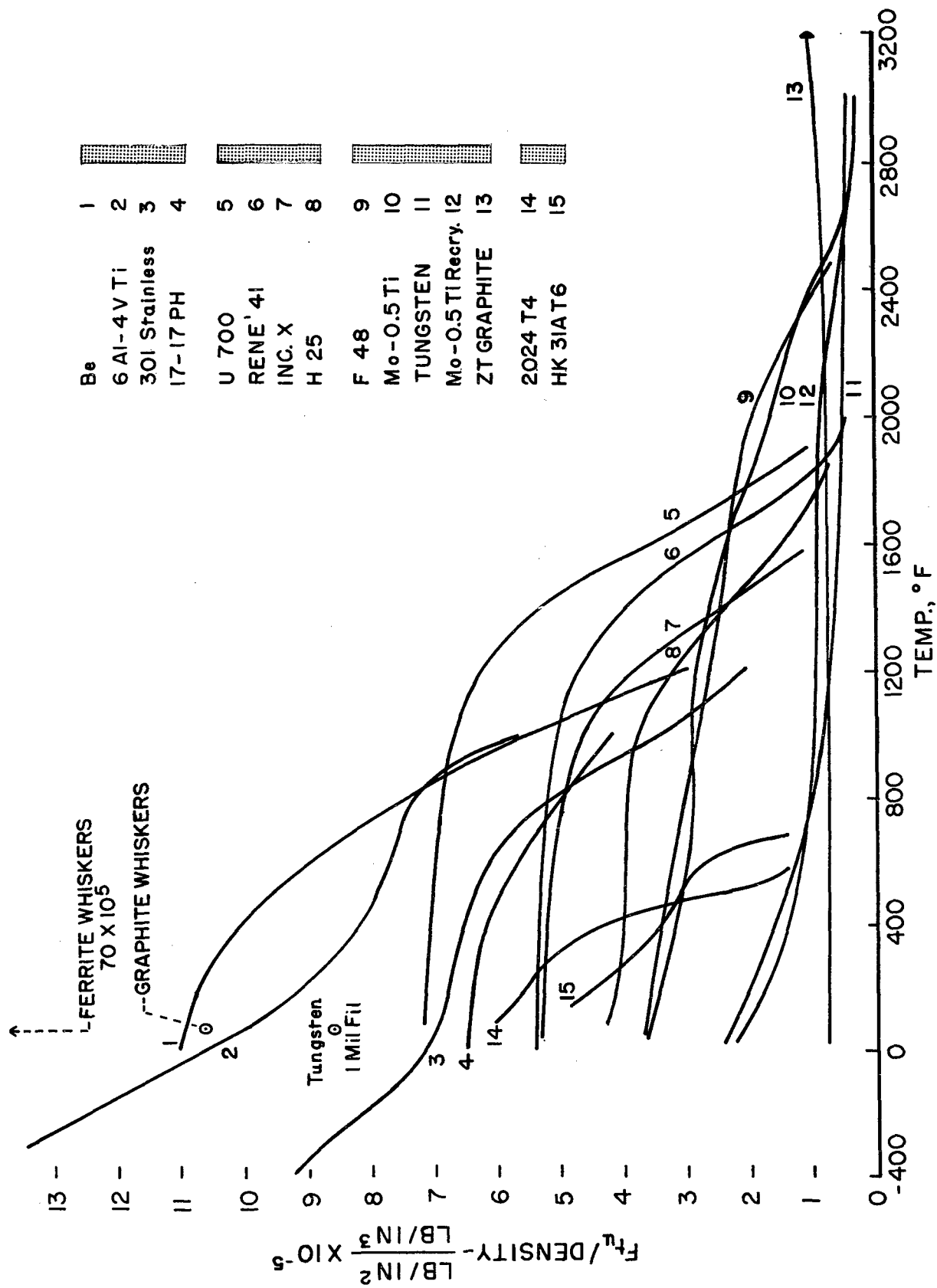


Figure 1.

STRENGTH-TO-WEIGHT RATIOS FOR 10,000 Hr.

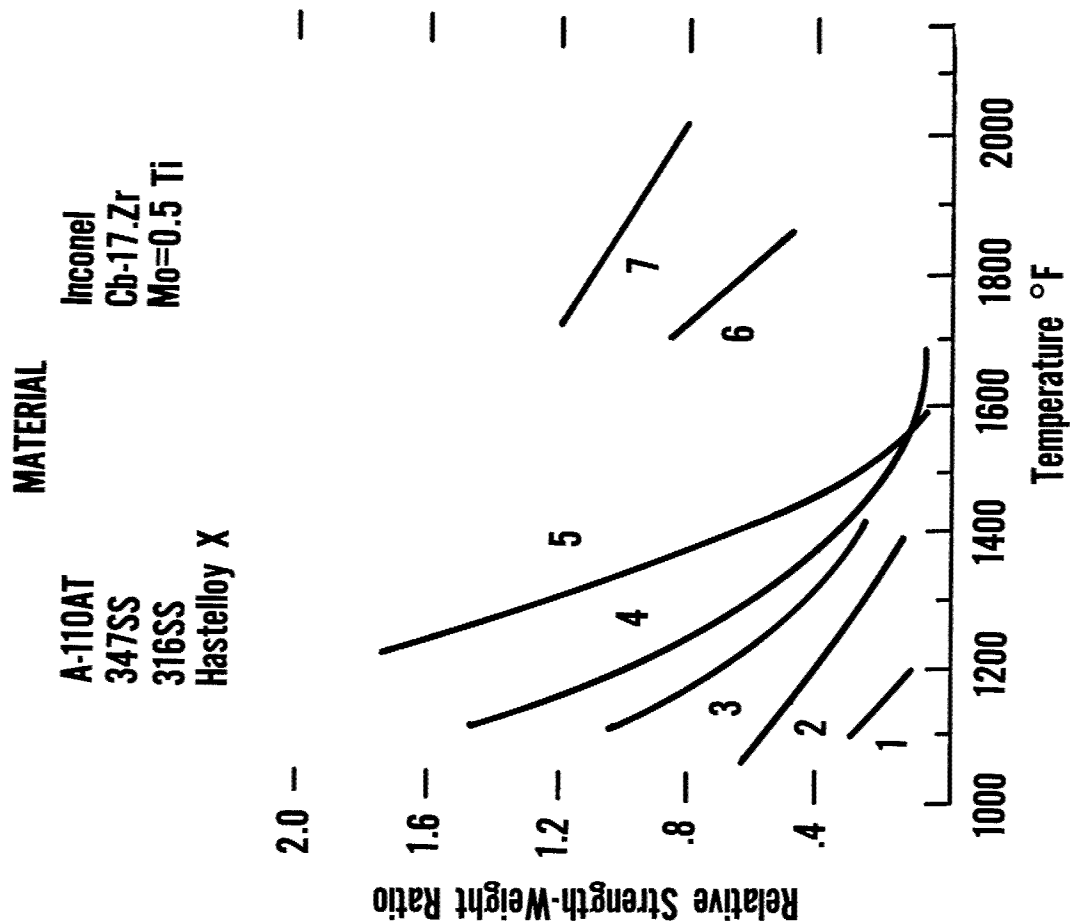
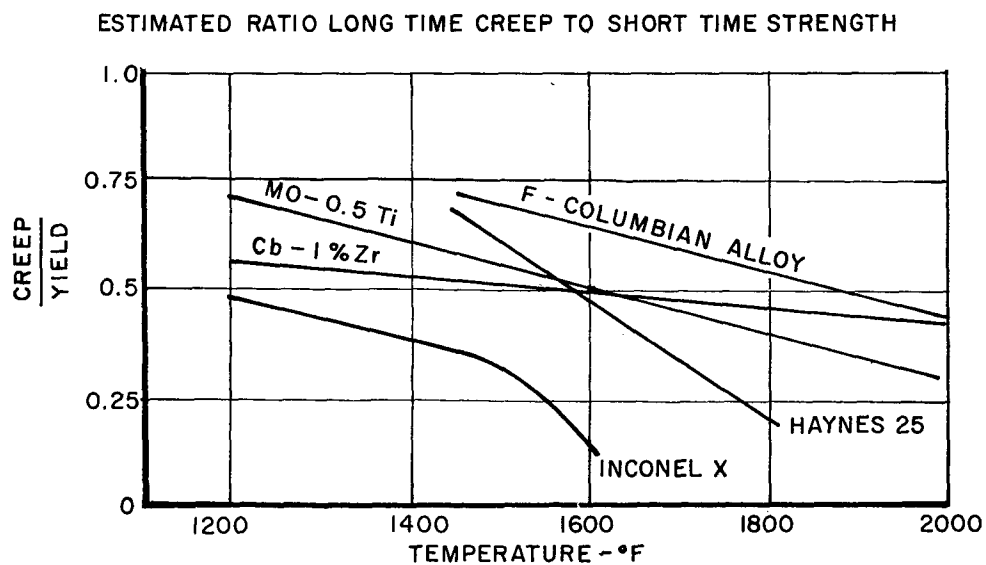


Figure 2.



NOTE :

CREEP = STRESS RUPTURE VALUE AT 0.2% CREEP AT
n HOURS, WHERE n VARIES FROM 100 HRS.
TO 1000 HRS.

YIELD = STRESS VALUE AT YIELD STRENGTH.

Figure 3.

WORKING FLUIDS & COOLANTS

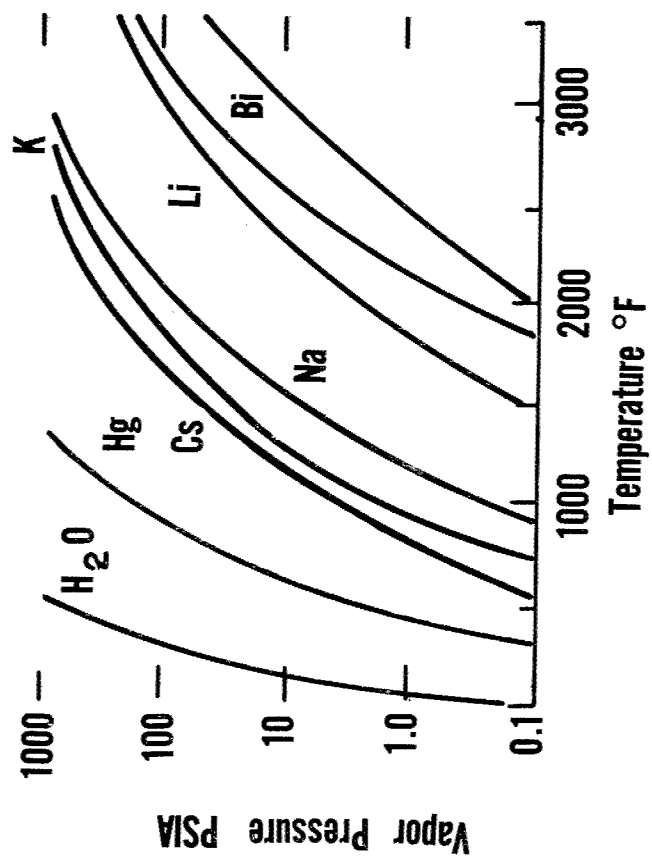


Figure 4.

MAJOR COMPATIBILITY PROBLEMS IN THE FLUID CYCLE

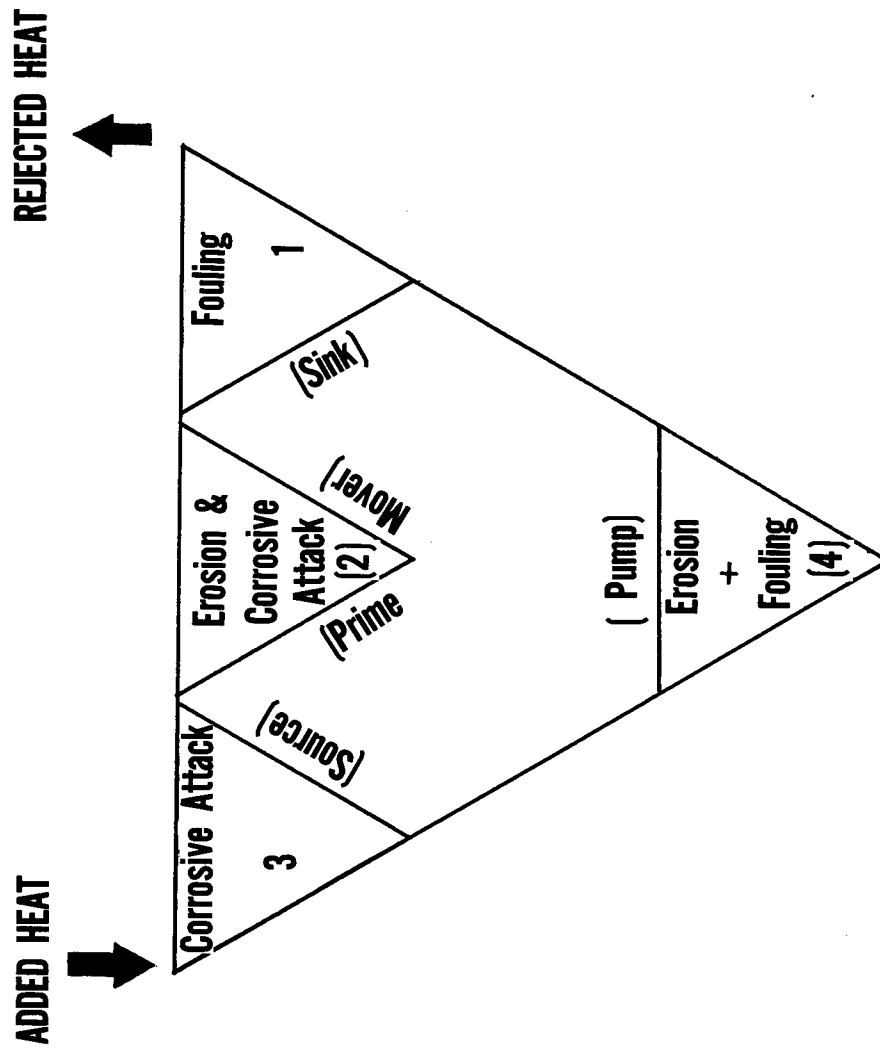
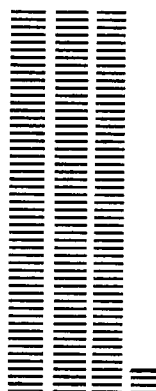


Figure 5.

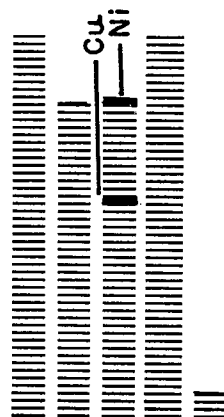
MATERIALS COMPATIBILITY WITH LIQUID RUBIDIUM

Temperature °F In Hundreds
0 2 4 6 8 10 12 14 16 18 20 22 24 26

Ferritic Stainless Steels 400 Series
Austenitic Stainless Steels 300 Series
Low Iron High Nickel Inconels
Pure Iron



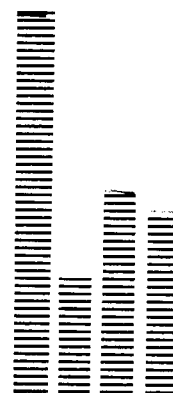
Cobalt And High Cobalt Alloys (Stellites)
Beryllium
Nickel, Copper And Their Alloys
Titanium And Vanadium
Zirconium



Molybdenum
Columbium
Tungsten



Brazing Metals Ni-Mn, Ni-Mo, Ni-P
Silver Brazing Alloys
Noble Metal Brazing Alloys Pt, Pd, Etc.
Aluminum And Aluminum Alloys



Aluminum Oxide
Beryllium Oxide
Graphite (Mono-Metal System)



Figure 6a.

MATERIALS COMPATIBILITY WITH LIQUID LITHIUM

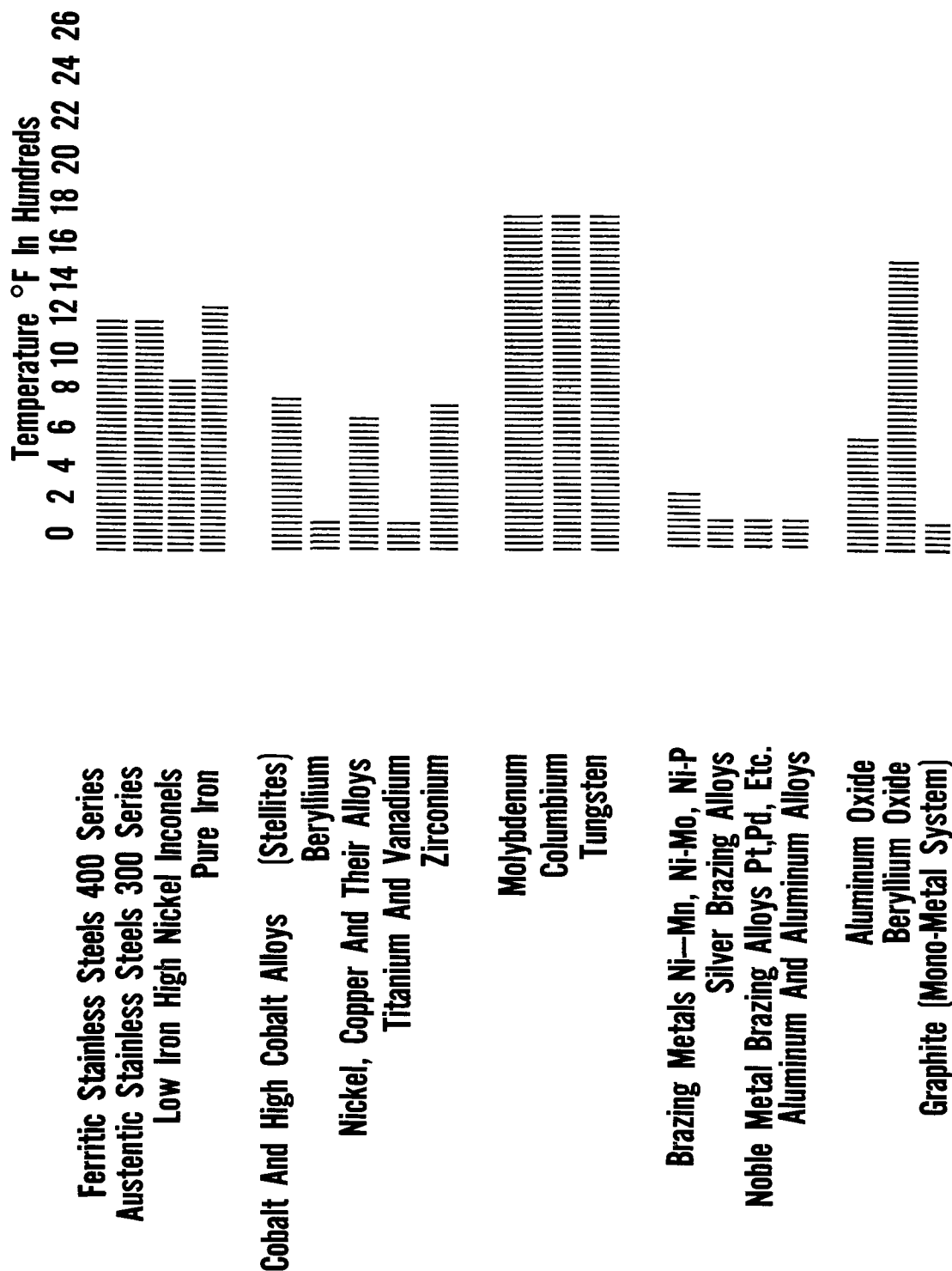


Figure 6b.

THE SOLAR ENERGY ABSORPTION OF THE DARK MIRROR COATING

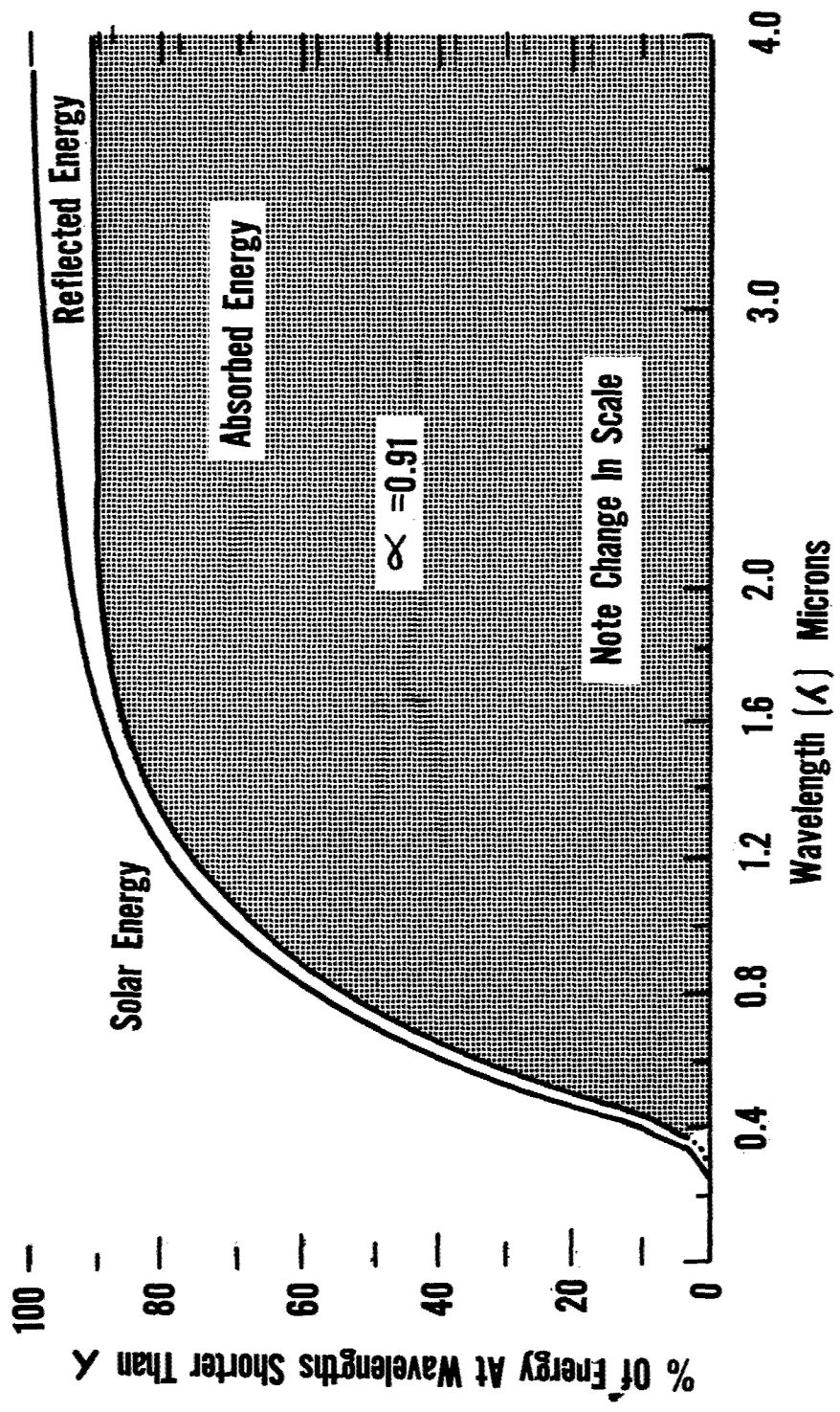


Figure 7.

THE INFRARED ENERGY ABSORPTION (OR EMITTANCE) OF THE DARK MIRROR COATING

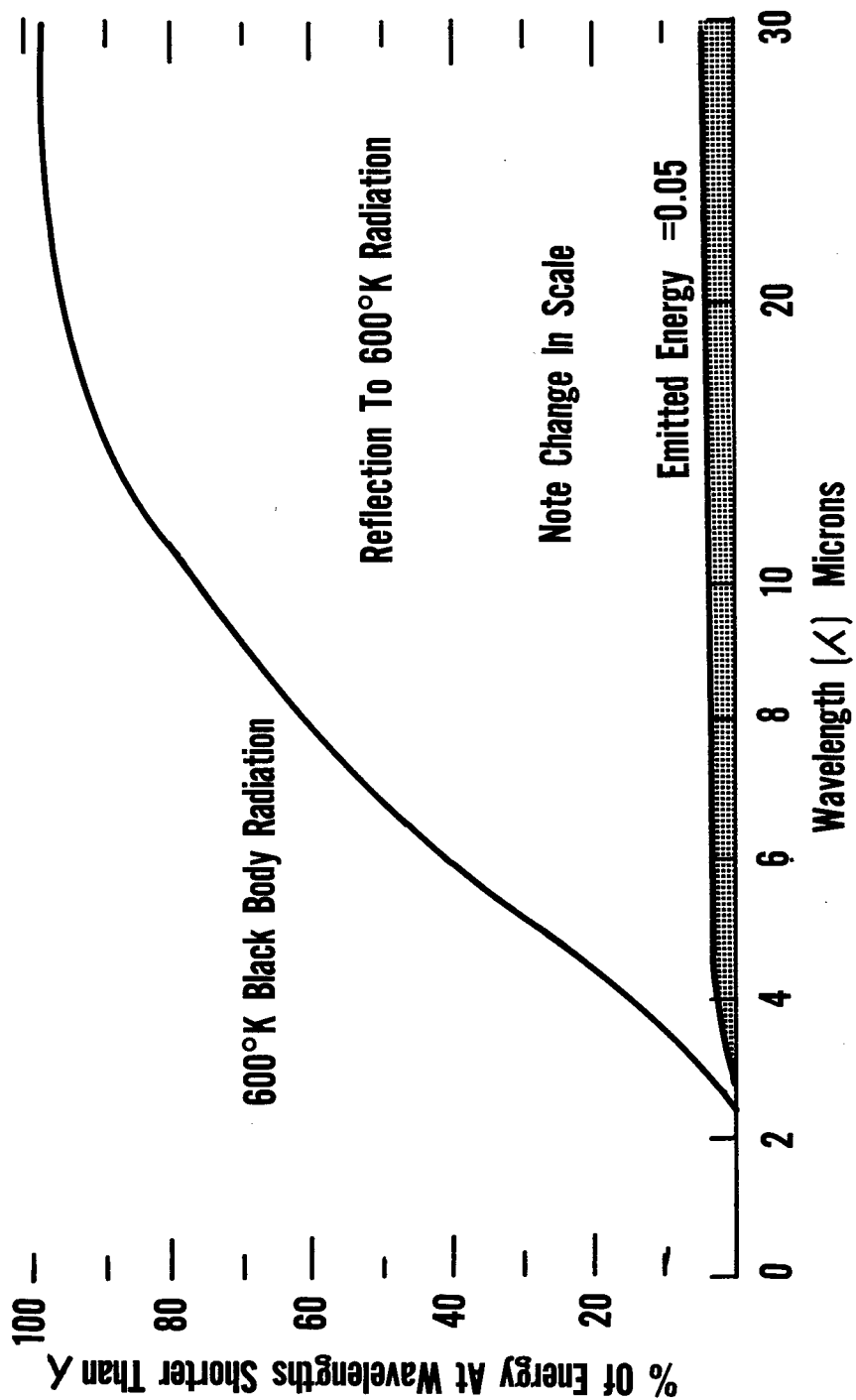


Figure 8.

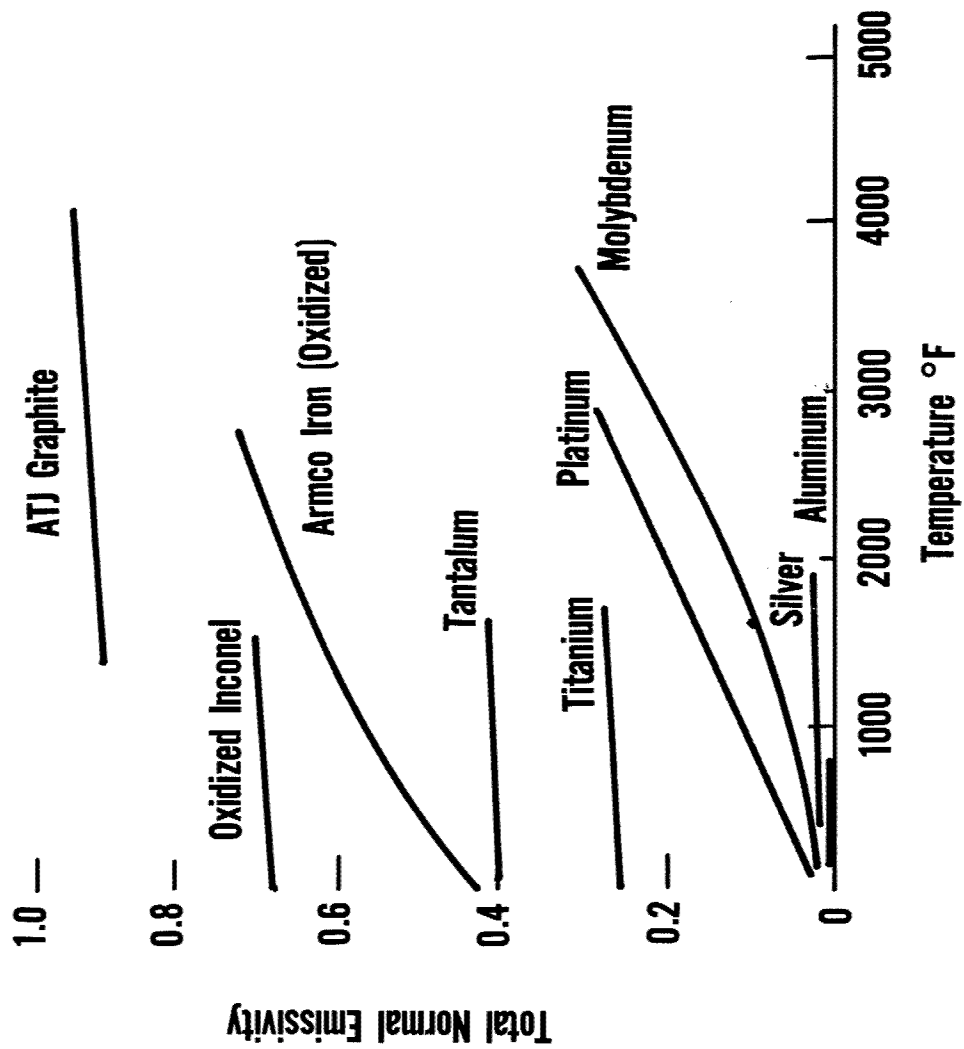
TOTAL NORMAL EMISSIVITY VS. TEMPERATURE

Figure 9.

TOTAL NORMAL EMISSIVITY VS. TEMPERATURE OF VARIOUS REFRACTORY MATERIALS

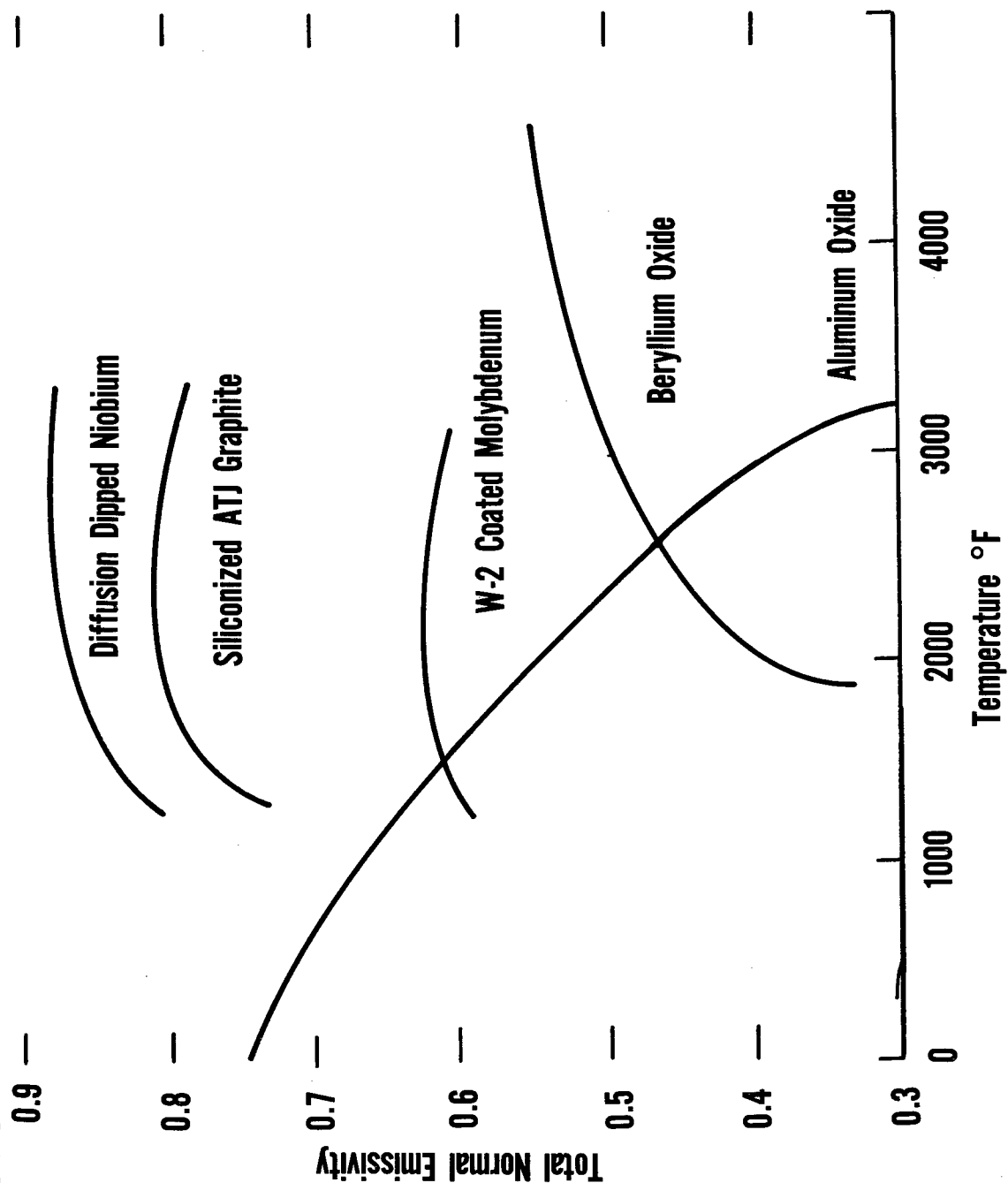


Figure 10.

LINEAR EXPANSION VERSUS TEMPERATURE

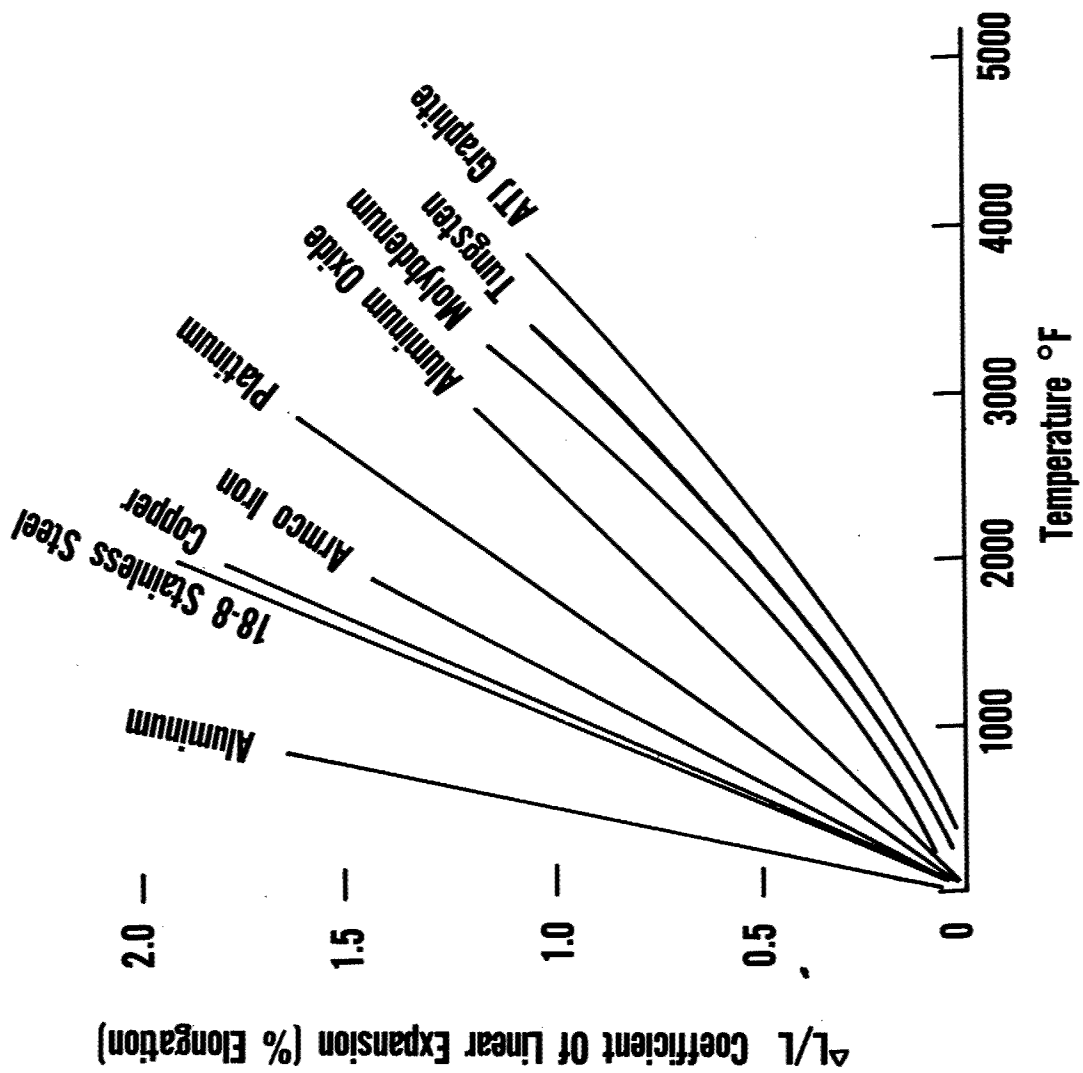


Figure 11.

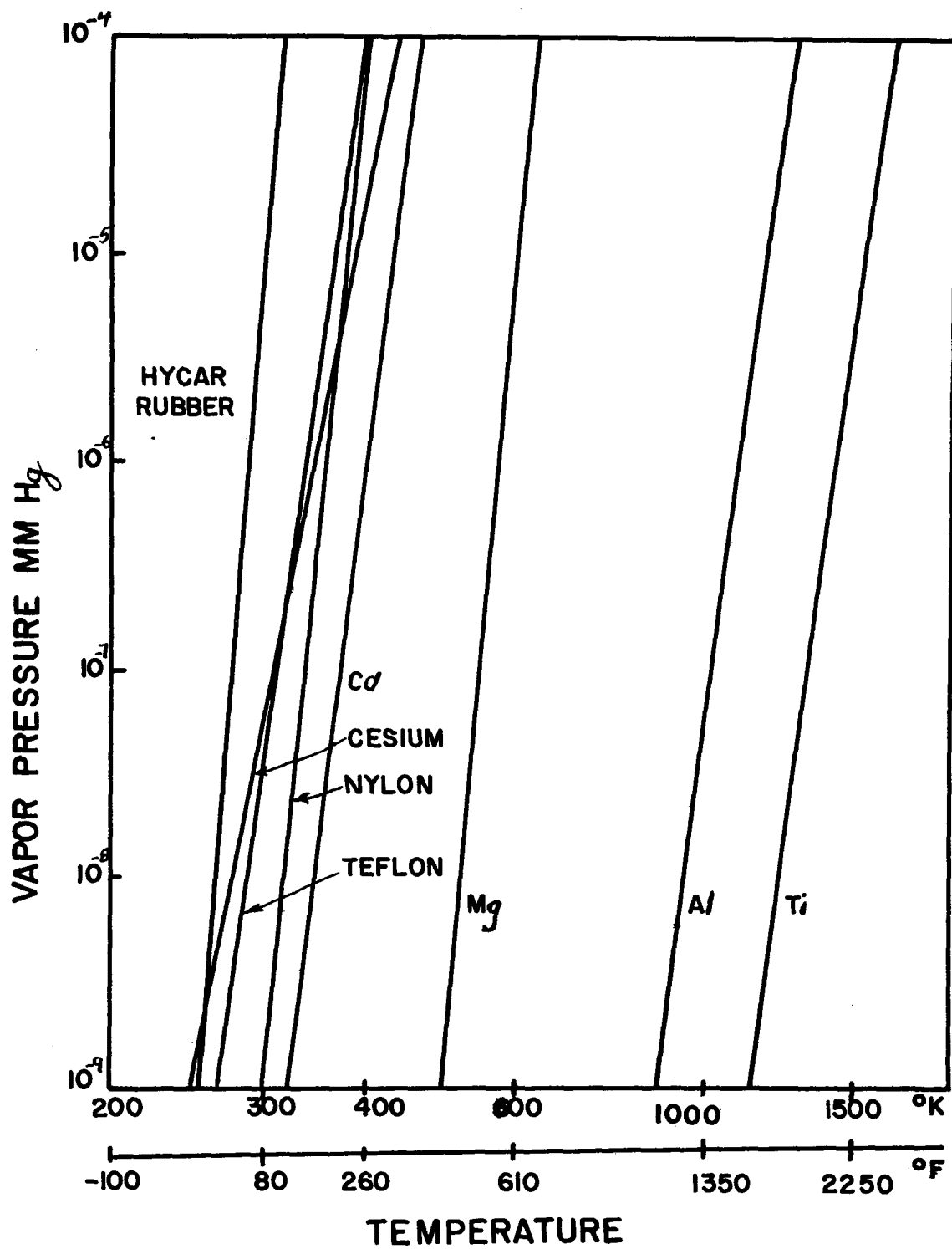


Figure 12.

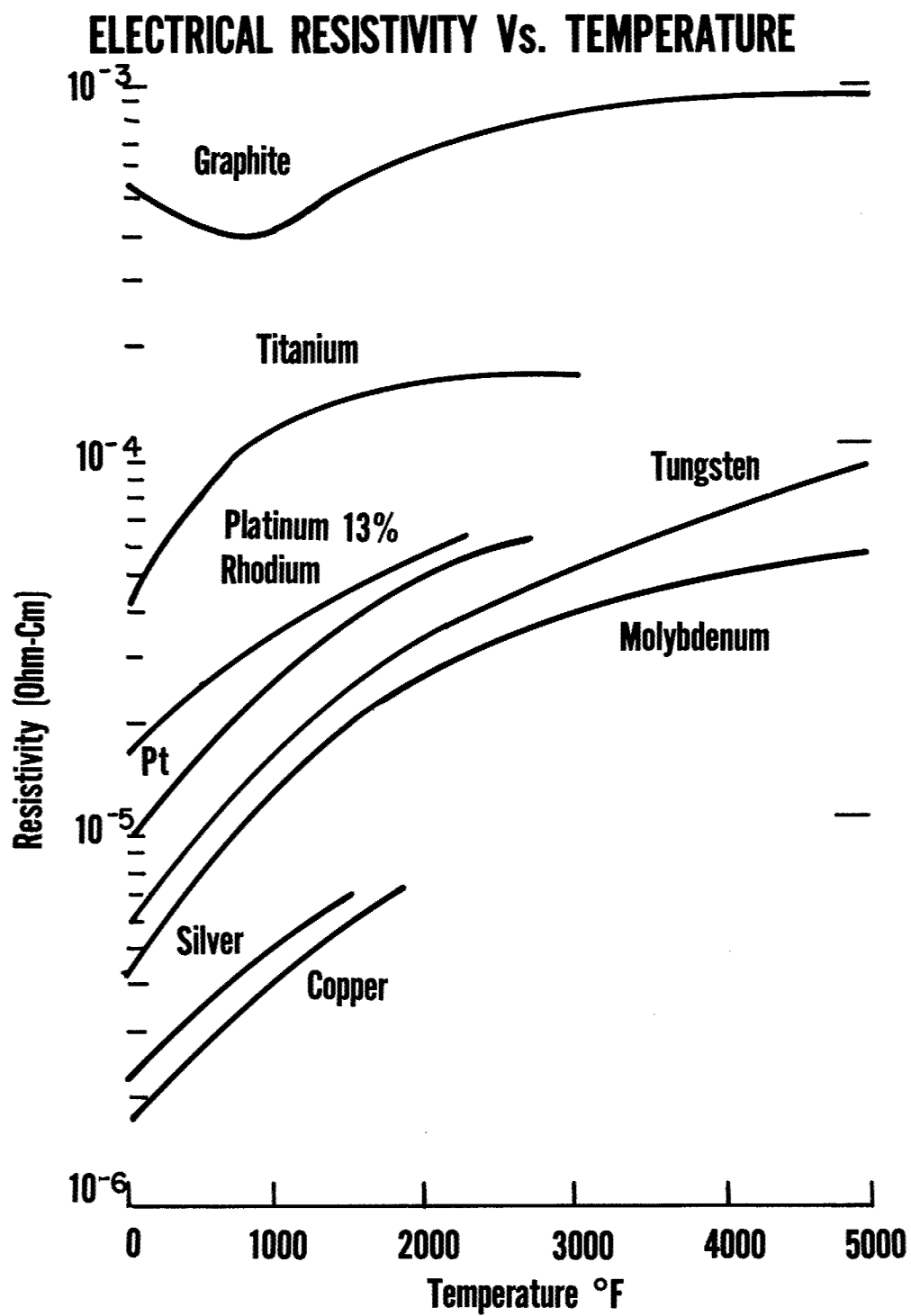


Figure 13.

MAGNETIC PERMEABILITY Vs. TEMPERATURE

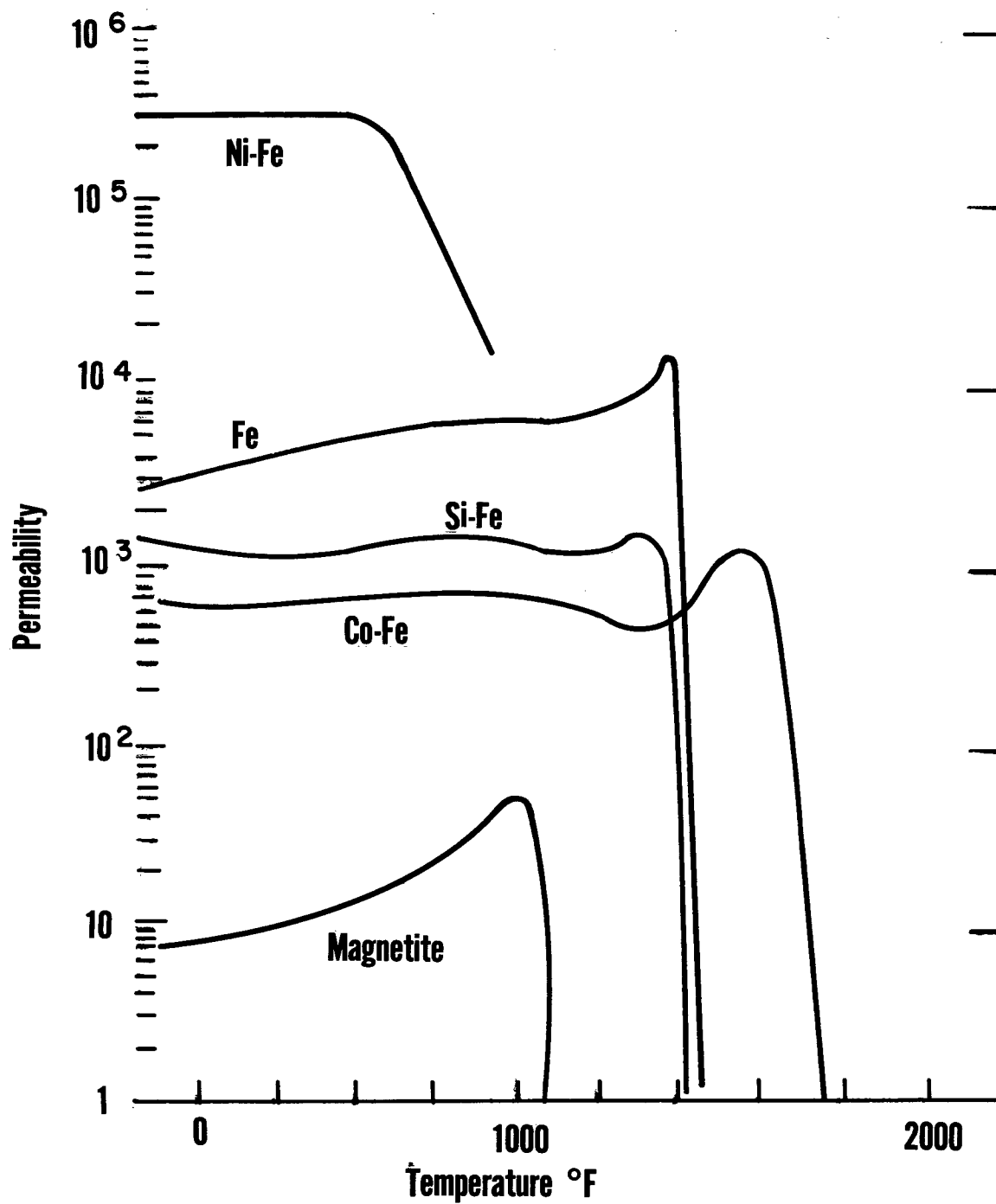


Figure 14.

FLIGHT VEHICLE POWER

Donald P. Mortel

Directorate of Aeromechanics, ASD

In my discussion I shall first define flight vehicle power, including a description of the methods to be employed for energy conversion. Subsequently, forecasted power requirements of the future will be discussed, including a forecast of the conversion methods that are considered most likely to be optimum for application to the various type future missions. Lastly, I will briefly present some of the power system materials problems that result from the space environment and the respective system operating features.

Flight vehicle power is defined as all that power necessary to operate any vehicle in flight, excluding the primary propulsion system but including the power required for electric propulsion and for extraterrestrial sites.

The power area is relatively broad, encompassing energy source technology; that is, techniques to convert energy to useful electrical, hydraulic, and pneumatic power, the transmission of this power to the load, as well as the conditioning of the power to make it compatible with the utilization equipment.

I will, however, deal only with the energy conversion techniques and the application of these techniques to the power requirements for typical future space oriented missions.

The advent of the space age has placed increasing emphasis on the exploration of new methods of converting energy to useful power. The power system must be self-sufficient, since we no longer can extract from the prime propulsion system, mechanically or otherwise, the needed power. In fact, if electric propulsion is to be employed in space vehicles, the propulsion system will be highly dependent on the power system. In addition, the requirements for power are expected to increase drastically in terms of power level, low specific weight, operating time, and reliability. Durations of 1000 hours will no longer be adequate; for in many cases, at least 10,000 hours of maintenance free, continuous, and reliable operation will be required.

The power level is expected to rise into the megawatt range.

Before going into the predicted future power requirements, a review of the energy sources available and the methods that can be employed in converting this energy to useful power is systematically explained in figure 1.

Figure 2 gives the schematic diagrams for some of the static conversion devices being considered:

a. Photovoltaic converter. A typical converter is a silicon solar cell. A material such as boron is diffused into one surface of the silicon crystal to form a very thin "p" layer with the original crystal in the opposite surface forming the "n" layer. Photon energy from the sun causes electron movement within the material from the "n" layer to the "p" layer of the material. With a suitable external circuit connected this movement of electrons does useful work.

b. The thermionic converter consists of two metal plates of different work functions. The cathode is a high work function material and the anode a low work function material. Heat energy is applied to the cathode, which causes electrons to boil off. These electrons collect on the anode, which has a lower work function, producing an electrical potential between the plates; thus, with a suitable load circuit the converter produces a flow of electrical current. Typical heat source and heat sink temperatures are 3000°F at the source and 1200°F at the sink.

c. The fuel cell converts chemical energy directly to electricity. In the example shown, hydrogen and oxygen are fed separately into the two electrodes. The two porous electrodes are separated by a KOH electrolyte. Under the influence of a catalyst in the hydrogen electrode, the hydrogen releases an electron. This electron flows through the load circuit to produce useful electric power and thus passes into the oxygen electrode reacting with the oxygen under a catalytic action to form water.

d. The thermoelectric generator is an adaption of the thermocouple which is used as a power generator instead of a temperature measuring device. In this case, heat energy is applied to the "n" and "p" type materials, resulting in a flow of electrons between the "n" leg and the "p" leg, creating a potential between the hot and cold junction, thus generating an electric current when the circuit is completed.

The devices just reviewed are categorized as static type generators. For this reason, they look very attractive from a reliability point of view.

The dynamic systems can utilize any of the three main energy sources discussed earlier, that is, nuclear, solar or chemical. The upper portion of figure 3 gives a block diagram of a chemical dynamic power system. The fuel is burned in a combustion chamber to generate hot gases which drive a turbine. The turbine, in turn, drives a generator or hydraulic pump to extract the power. In this case, the hot gases are exhausted overboard. If a reciprocator is used in place of a turbine, either internal or external combustion can be utilized. If cryogenic fuels are used, there is the possibility of using the fuel to provide a certain amount of environmental control or cooling prior to its entrance as a fuel into the power unit. Thus the penalty for the fuel volume and weight, which exists with chemical power units, can be partially charged to other subsystems and will result in a marked overall saving of weight.

In the case of solar or nuclear systems, the Rankine closed cycle is the most popular. There can be several variations of the Rankine cycle, namely, single loop, two loop, and three loop systems. On the lower half of figure 3 a single loop system is represented by the solid lines. Heat is applied from a solar collector or reactor to a boiler where boiling of a working fluid occurs. Vapor thus generated passes through a turbine which drives the alternator. The vapor is then condensed to a fluid in a radiator, after which the fluid is pumped again through the boiler. The dashed lines indicate the addition of a second loop where a fluid is used to cool the reactor. This fluid, after being heated by the reactor, is passed through the heat exchanger-boiler, where the second fluid is vaporized for use in the turbine loop. This vapor, after doing work in the turbine, is condensed in a radiator, thus making a two loop system. A third loop can be added as depicted by the dotted lines. In this case, a heat exchanger is used in lieu of a radiator in the turbine loop to condense the vapors by use of a third fluid. The waste heat picked up by the third fluid is then carried to a radiator for dissipation to space. All three versions have their advantages and disadvantages. Generally, however, a single loop system is favored in a solar power unit and a multiple loop system is favored in a nuclear power unit.

There is one consideration, however, that is common in both the solar and nuclear systems, radiation at as high a temperature as is possible. The reason: the amount of heat which can be radiated to space per unit area is proportional to the fourth power of the temperature of the radiating surface. Since the overall cycle efficiency of these systems is rather low, a large amount of waste heat must be dissipated, and therefore the radiator becomes a major part of the system weight and volume. This is particularly applicable to the large nuclear system. To give an example of the effect that the radiator temperature has on radiator surface area, compare a 300 kilowatt Rankine machine radiating at 700°F with one radiating at a temperature of 1200°F. At 700°F the radiator surface area would be approximately 1890 square feet as compared to 485 square feet when radiating at 1200°F. Hence, the radiator area could be reduced by nearly a factor of 4 by going to the higher temperature. It is for this reason that a great deal of emphasis has been placed on investigating such fluids as rubidium, potassium, sodium and lithium as the working fluids, to permit operation at very high cycle temperatures and yet retain reasonable cycle thermal efficiencies. This is especially true for the high power output machines (above 100 kilowatts).

Now, let us examine the trends of requirements for power for various types of typical missions, and the types of power conversion systems which are expected to be most optimum to fulfill these forecasted requirements in the 1962 and 1966 time period.

Figure 4 represents a synthesized forecast of the electrical load requirements for various types of general missions in the 1962 time period, plotted against the duration that the load or power will be required. Keep in mind when reviewing all of the remaining figures that the lines do not represent firm boundaries but should be looked at as bands, since there is considerable overlap between areas.

a. Boosters are expected to require powers ranging from a few watts up to 70-80 kilowatts, but the duration for which the power is needed is low; ranging from a few seconds up to a few minutes.

b. Boost glide and unmanned air vehicles will require 10 to 100 kilowatts, with duration measured in hours.

c. Earth satellites require power ranging from a few watts up to approximately 30 kilowatts, with durations ranging from hours to years.

d. Lunar vehicles by the 1962 period will probably not need over 5 kilowatts of power as the maximum. The time duration will range from 1 day to 6 months.

e. Interplanetary vehicles, if they exist in the 1962 to 1966 period, will probably need no more than 1 kilowatt of power. However, the minimum duration for the power system will be 6 months on upward into years.

Figure 5 is the forecast for 1962 of the optimum application of energy conversion methods when considering minimum system weight. From this we can see that the battery can fulfill the needs for power of 1 kilowatt for 1 minute duration to 100 watts for 1 day duration. The chemical dynamic systems will provide the power for systems requiring up to 100 kilowatts for periods of 1 day to 1 week. You should note that the cryogenic type system is expected to fulfill the 1 week requirement. The fuel cell will also compete for durations of 1 day to a couple of weeks for power levels of about 7-8 kilowatts. For the long duration missions extending into years, the photovoltaic systems have been and will continue to be favored for power levels up to from 500 to 600 watts, with solar thermionic

systems expected to be the most optimum for power levels of from 500 watts up to 5 to 6 kilowatts. Above this level, up to about 30 kilowatts, the solar dynamic systems will be most competitive. It should be noted that the dynamic systems are considered to have a major life and reliability hurdle at about the 1 year level.

Figure 6 is an overlay of figures 4 and 5 to permit the formation of a mental picture of which power systems will fit the various types of projected missions. The solid lines represent the mission power requirements of figure 4 and the dashed lines represent the conversion methods of figure 5. It is evident that the battery and chemical dynamic systems of the hydrazene type can fulfill the requirements for boosters. The cryogenic chemical dynamic systems will dominate for the unmanned air vehicles and boost glide and glide re-entry type vehicles. Fuel cells, thermionics, and photovoltaics will be the competing power systems for lunar vehicles, depending on the specific power level and the length of mission required. The earth satellites, again depending on the specific power requirement and duration, will be able to use fuel cells, photovoltaics, solar thermionics, or solar dynamic type systems. The power requirements for the early projected interplanetary vehicles will probably rely on photovoltaics or solar thermionics to fulfill the long duration projections shown.

Looking into the 1966 and later periods, figure 7 is a forecast of the power levels required for missions expected in that era. Generally the power levels are expected to increase markedly for each type mission, with new requirements added for the recoverable boosters and lunar and space station type missions. It is well to note that the power requirements for lunar and space stations and for interplanetary vehicles are expected to reach approximately 10 megawatts, and durations of two years or more.

Figure 8 is the forecast of the optimum conversion methods expected in the 1966 period for various power levels and duration requirements. This chart shows that the power level capability of cryogenic dynamic systems and fuel cells is expected to increase by an order of magnitude from the 1962 capability, and the large nuclear dynamic system now appears.

Looking at figure 9, which is an overlay of figures 7 and 8, and examining the mission power requirements for 1966 against conversion method capability, one can see that the battery, hydrazene and cryogenic chemical power units are expected to fulfill the booster power requirements. The cryogenic dynamic power systems will also be optimum for recoverable boosters, unmanned air vehicles, and the boost glide type vehicle, with the fuel cell as a possible contender in the boost glide type vehicle. The requirement for power for lunar vehicles and earth satellites, depending on specific vehicle power level requirements and duration requirements, will be met by fuel cells, photovoltaics, solar thermionics or solar dynamics. The fuel cell is expected to cover the requirements for missions of from 1 day to 6 months for power levels up to 20-30 kilowatts, with the missions of more than six months requiring photovoltaic systems, solar thermionic systems, or solar dynamic systems, depending on the power level. For those requirements over 30 to 40 kilowatts, the nuclear dynamic system will be required. The nuclear thermionic system, which has a possibility of being competitive in the 100 kilowatt level by 1966 is not shown on the chart.

For lunar stations, space stations, and interplanetary vehicles, there is little doubt that the nuclear dynamic system will be the major contender in the 1966 time period. For periods later than this, the static type nuclear thermionic converter may play some role for this type of vehicle.

As the last part of my discussion, I would like to touch briefly on materials problem areas on some of the power units that require significant applied research attention. Specifically, these include the nuclear and solar dynamic conversion systems, the thermionic converter, the fuel cell and finally rechargeable batteries.

Aside from the inherent reliability problems of devices with moving parts, the nuclear and solar dynamic systems are today characterized by undesirably large components. This is a result of low system efficiencies and low operating temperatures. For the solar powered system, the solar energy collector is the largest component and reduction in collector diameter is essential. Small collectors are desirable: (a) to minimize storage volume in the payload package during launch, (b) to make practical the fabrication of optically-accurate mirrored surfaces, (c) to reduce the aerodynamic drag on space vehicles in low altitude orbits and (d) to minimize the probability of micrometeoritic damage to the collector-mirror surface. An increase in the overall system efficiency is the obvious answer to collector size reduction; however, this is almost inevitably achieved at the expense of higher system operating temperatures.

For the large nuclear powered dynamic system, the radiator system is of major concern. It is predominantly the largest, and heaviest, single component. This characteristic, coupled with the fact that it is a fluid-carrying component, makes the entire system extremely vulnerable to failure by micrometeorite damage. Therefore every attempt should be made to radiate waste energy at as high a temperature as possible so that the radiator size may be drastically reduced. Again, the high radiator temperature reflects correspondingly higher temperatures upstream, in the system, in order to maintain reasonable system efficiencies. The trend toward higher system operating temperatures, eventually forces the designer to substitute water and mercury, the more conventional Rankine cycle working fluids, with fluids such as the alkali metals. (That is, rubidium, potassium, sodium etc.) However, the combination of these high-chemically reactive fluids, and high operating temperatures introduces severe problems of thermal stress, corrosion, mass transport phenomena of containment, and structural materials. Refractory materials appear to have promise but are relatively new and unproven.

Turning to some of the problems with the static methods of energy conversion, the first significant area is that of the thermionic converter. It operates at extremely high temperatures. Further, an easily ionized but highly chemically reactive gas, cesium, is used to neutralize space charge. Problems created by this chemical reactivity are: an undesirable rate of cathode material evaporation, high temperature hermetic seals, and with structural, joining, and containment materials. Corrosion problems are also caused by the cesium vapor.

With respect to fuel cells, the most significant problem is that of obtaining suitable electrode materials to prevent "flooding." More specifically such "flooding" prevents the cell electrolyte from entering the porous electrodes, thus stopping the necessary chemical reaction from occurring.

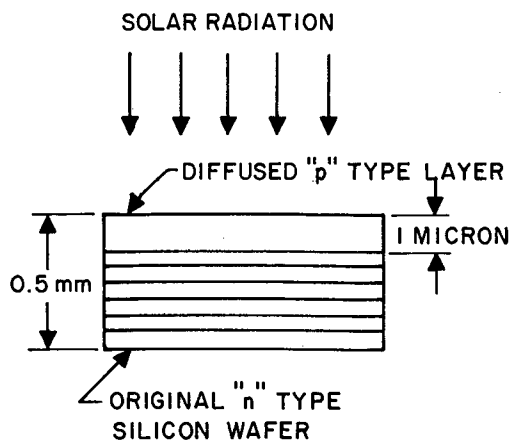
The last power unit that I would like to cover is the rechargeable storage battery, those batteries used as energy storage devices for static solar power systems to provide continued electrical power to the satellite during "orbit-shadow." Nickel-cadmium batteries are the most widely used for this purpose at the present time; however, the problems of separator deterioration, temperature sensitivity and most important, low theoretical efficiency, are sufficient inducement to lean toward other types. For example, a watt-hrs/lb increase of four to one is theoretically possible with the silver-zinc battery as compared with the nickel-cadmium. The problem, however, with the silver-

zinc battery is that silver migrates from the positive to negative electrodes. Theoretically, twelve to one increase in watt-hrs/lb is possible with fused salts, such as the Alkali-Alkaline Oxides. However, severe corrosion of containment materials is still a problem.

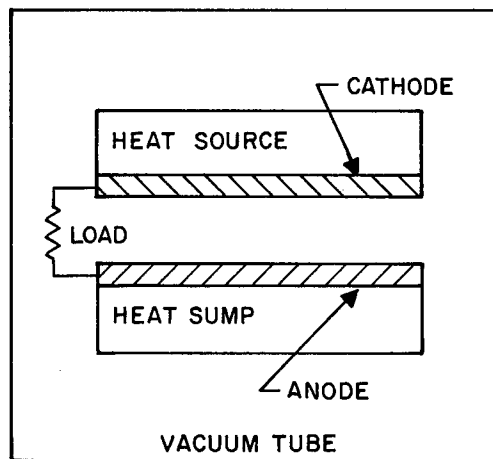
In conclusion, the energy conversion methods that are expected to be employed to fulfill projected mission requirements, whether static or dynamic, are relatively new and unproven. Serious problems face the system designers in attaining high power density and compact devices that are compatible with the space environment. These problems are only challenges. As in the past, research will bring to light not only many new materials but many new material systems as well. Problems are not just problems; they are challenges to be overcome.

ENERGY SOURCE	CONVERSION DEVICE	VARIATIONS
CHEMICAL	DYNAMIC POWER UNITS	(A) OPEN CYCLE
		(B) POSITIVE DISPLACEMENT DEVICES
		(C) COMBINATION OPEN AND CLOSED CYCLE
SOLAR	FUEL CELLS	(A) PRIMARY
		(B) REGENERATIVE
	BATTERIES	(A) PRIMARY
		(B) RECHARGEABLE
	PHOTOVOLTAIC	(A) SOLAR CELLS
		(B) PHOTOEMISSION
NUCLEAR	THERMIONICS	
	REGENERATIVE FUEL CELL	(A) STIRLING CYCLE
	DYNAMIC MACHINERY	(B) CLOSED RANKINE CYCLE
	THERMIONIC	
	THERMOELECTRIC	
	REGENERATIVE FUEL CELL	(A) CLOSED RANKINE CYCLE
	DYNAMIC MACHINERY	

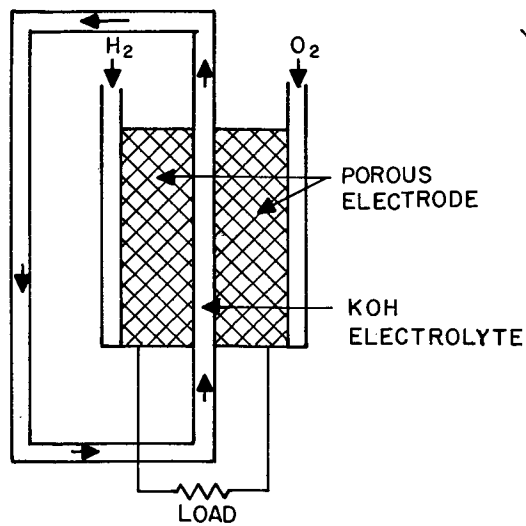
Figure 1.



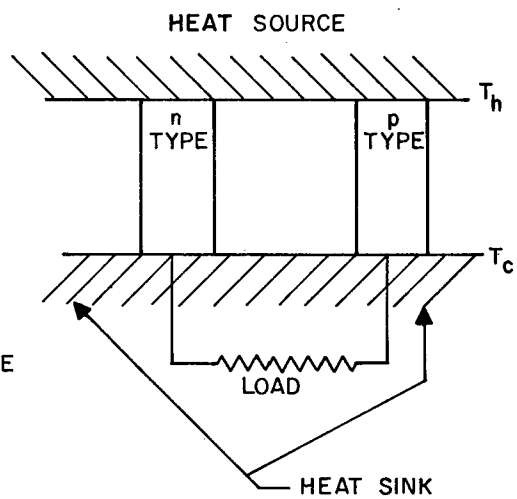
(a) SILICON SOLAR CELL



(b) THERMIONIC CONVERTER



(c) FUEL CELL



(d) THERMOELECTRIC CONVERTER

Figure 2.

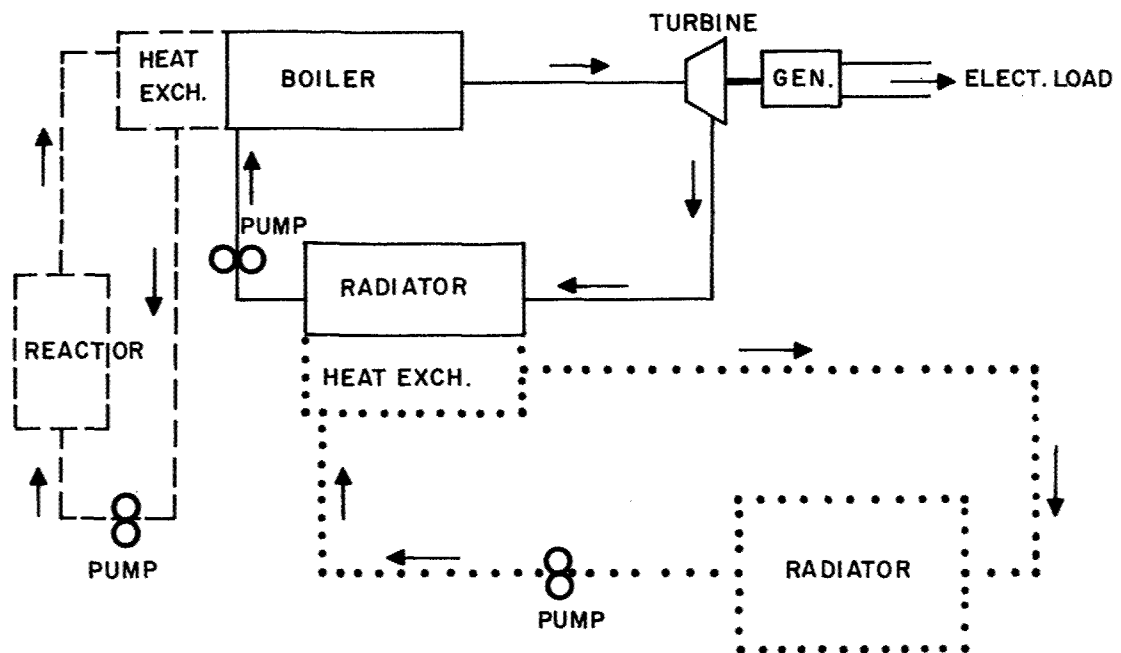
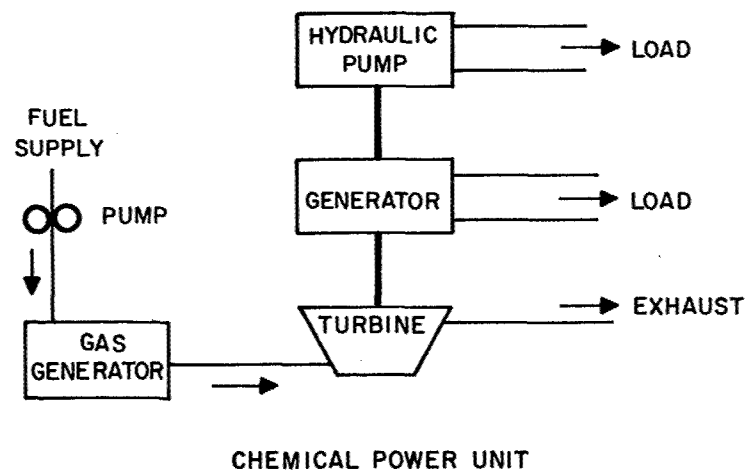


Figure 3.

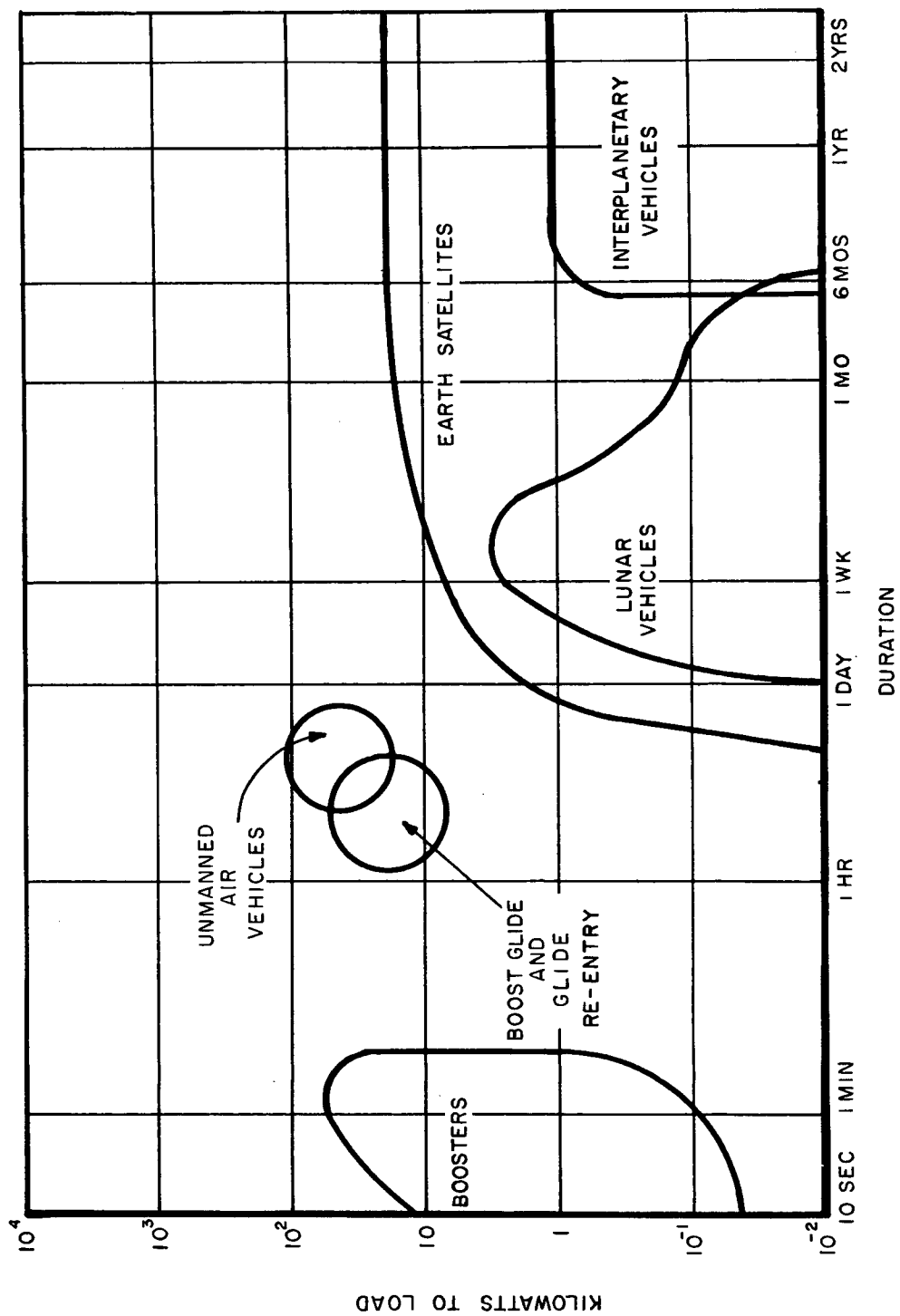


Figure 4. Synthesis of Forecasts of 1962 Requirements for Flight Vehicle Power

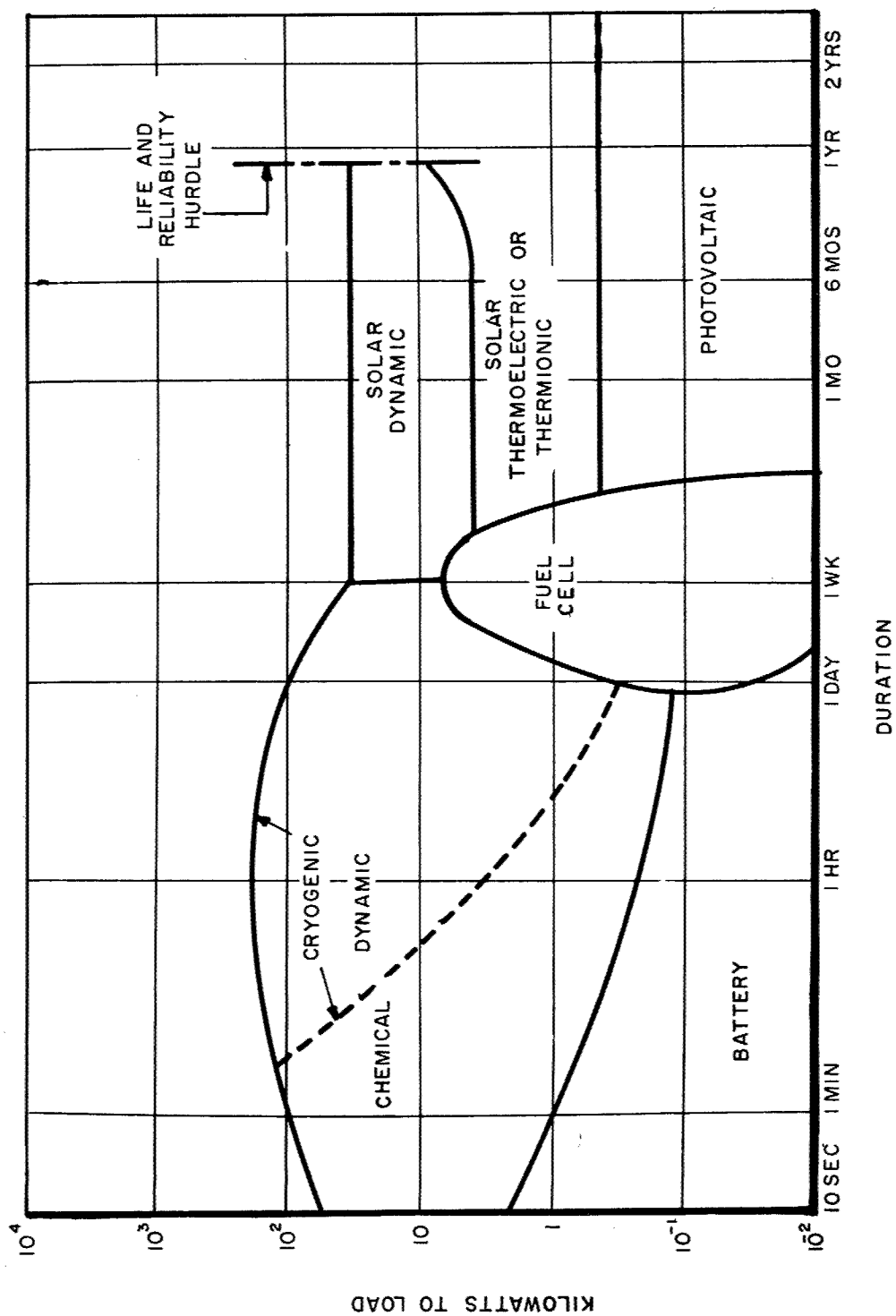


Figure 5. Synthesis of Forecasts of 1962 Areas of Optimum Application of Energy Conversion Methods

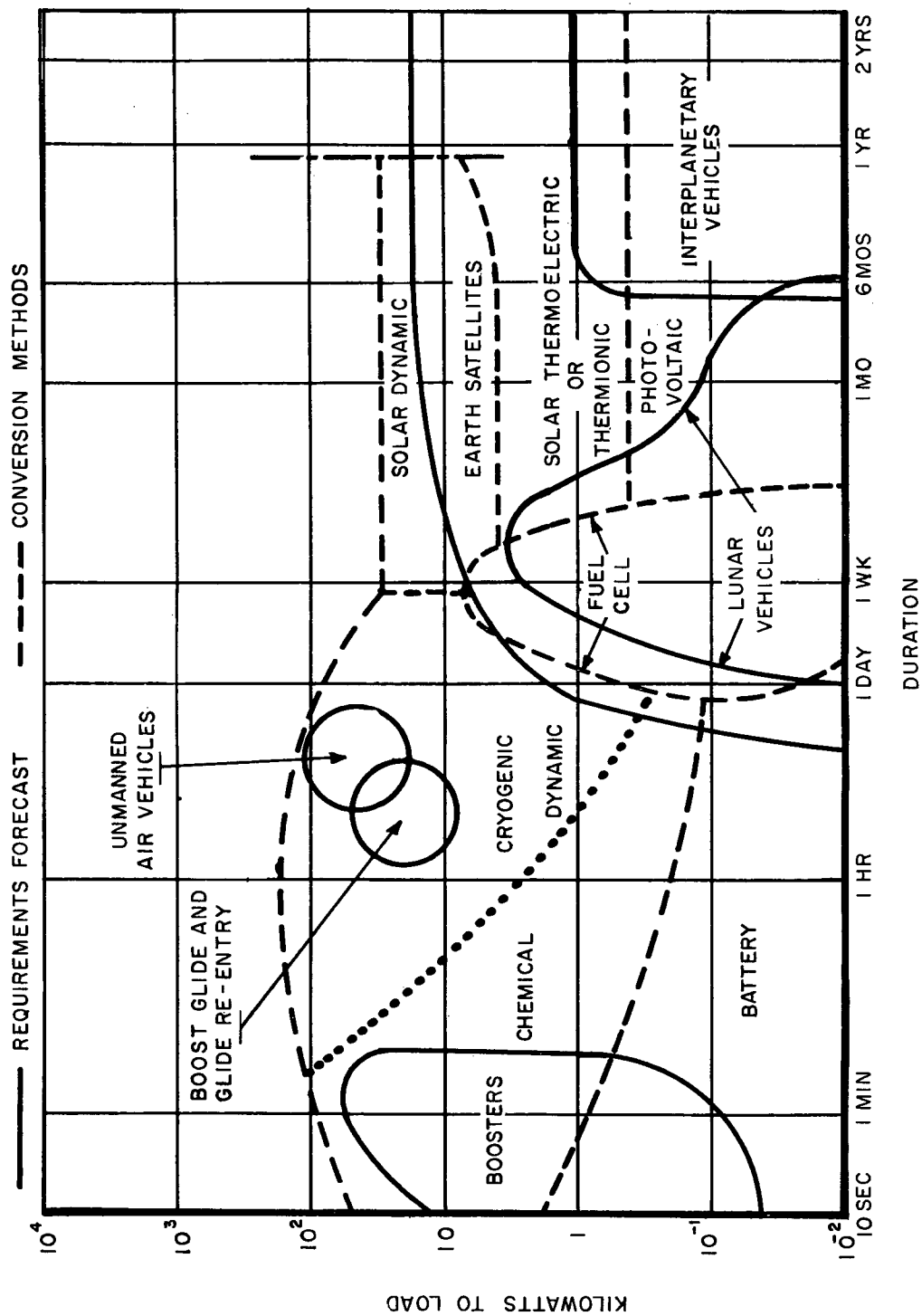


Figure 6. Overlay of 1962 Forecast Requirements and Energy Conversion Methods

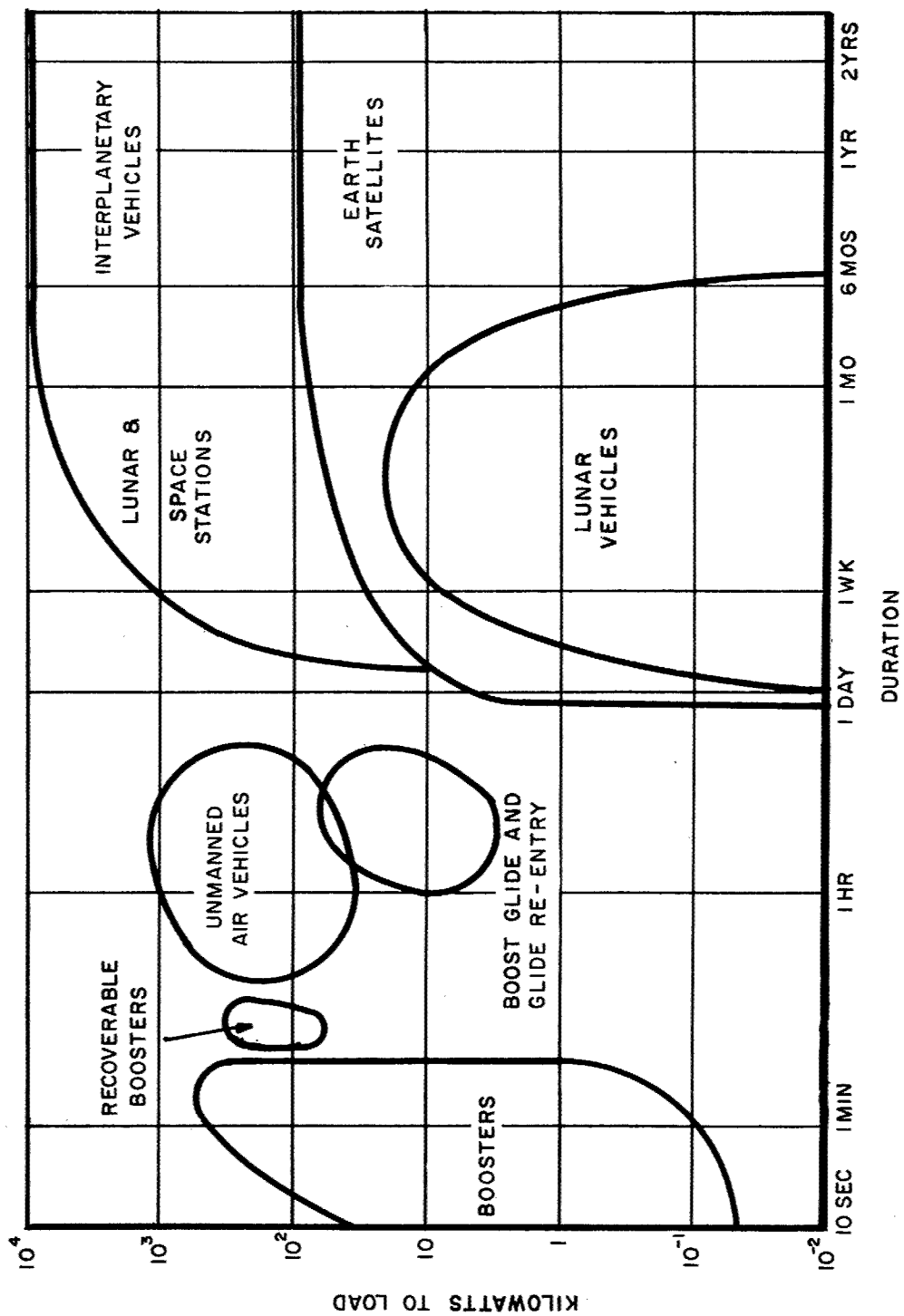


Figure 7. Synthesis of Forecasts of 1966 Requirements for Flight Vehicle Power

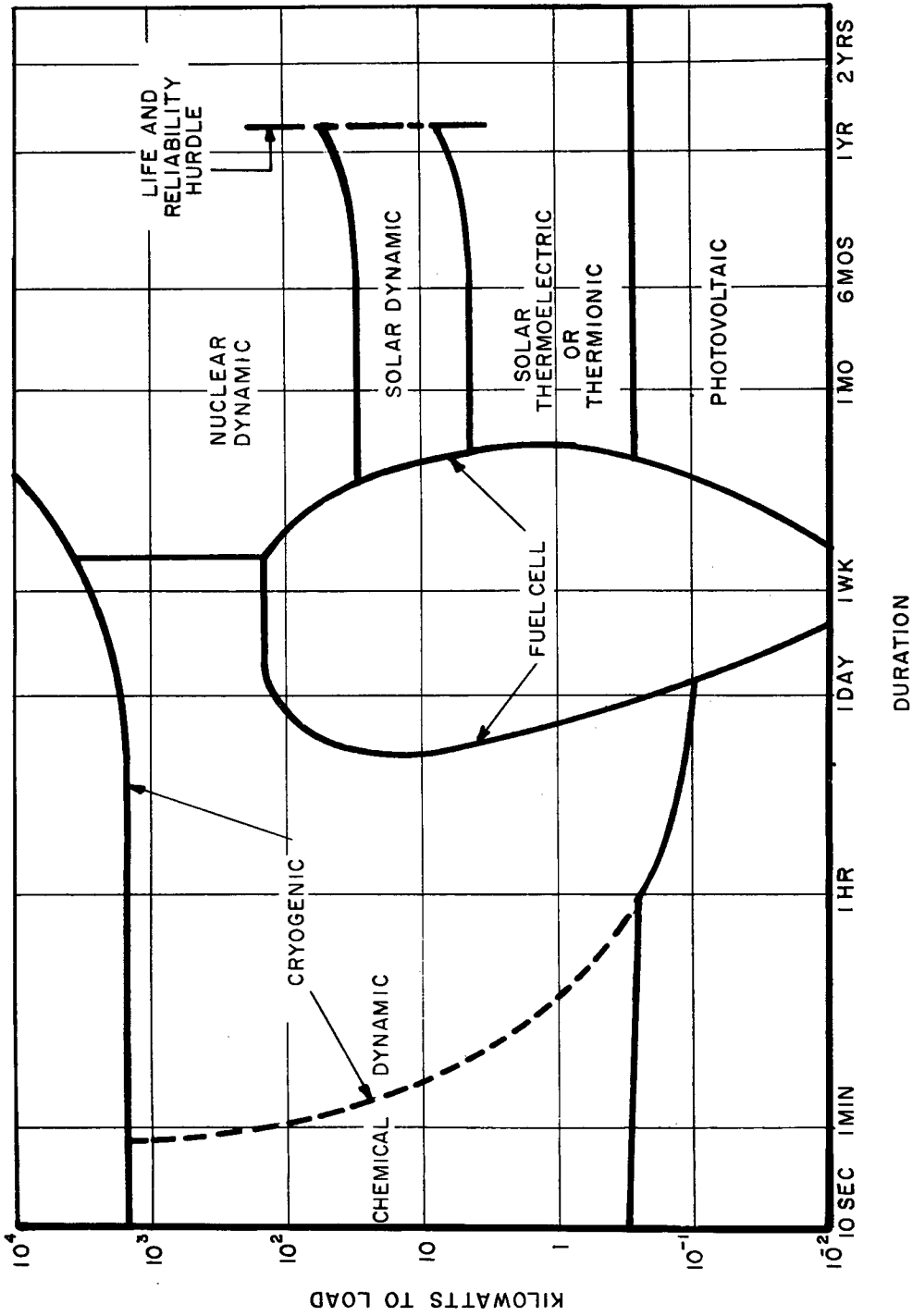


Figure 8. Synthesis of Forecasts of 1966 Areas of Optimum Application of Energy Conversion Methods

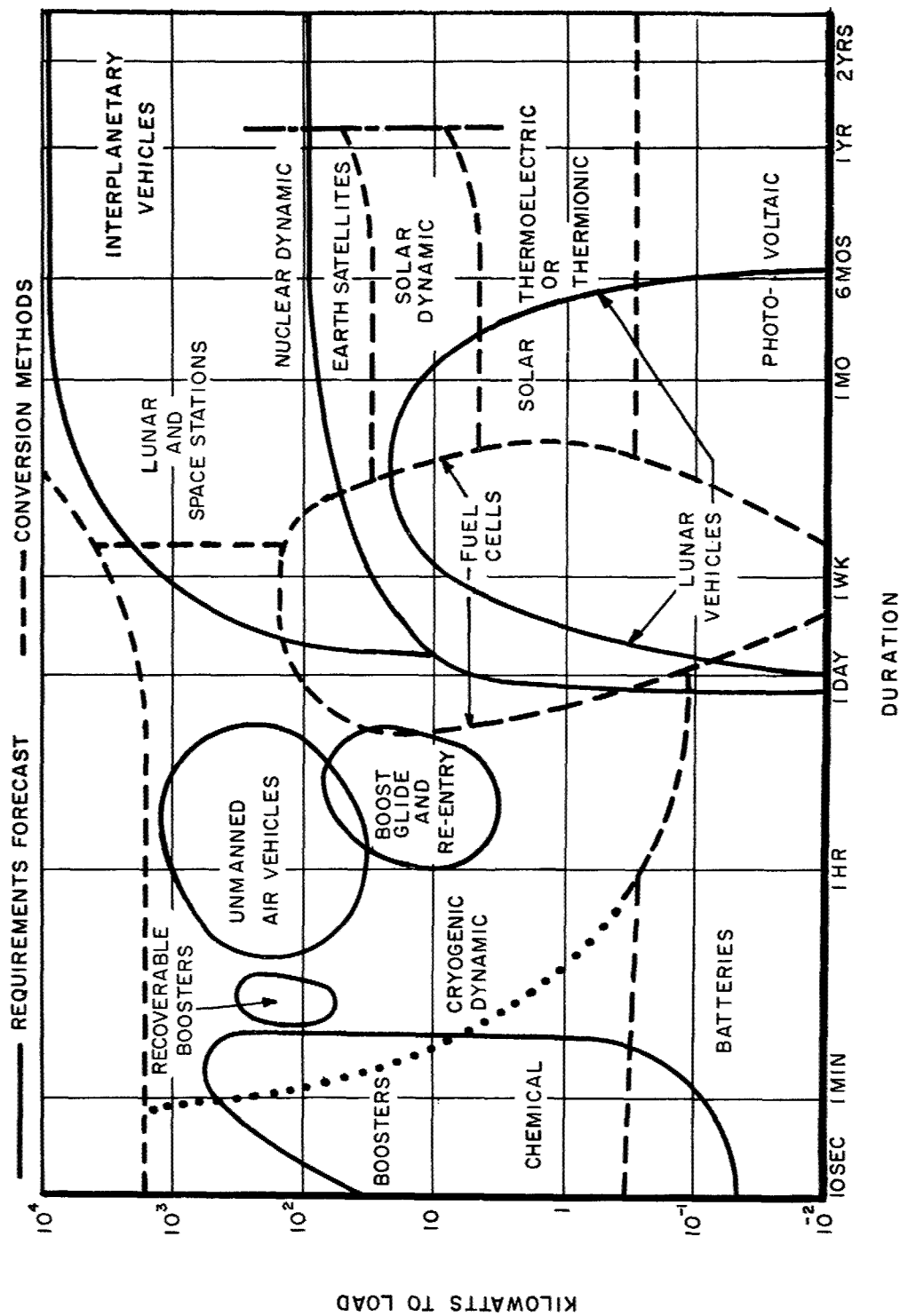


Figure 9. Overlay of 1962 Forecast Requirements and Energy Conversion Methods

IMPROVING THE MUTUAL GUIDANCE AND SUPPORT BETWEEN THE FIELDS OF MATERIALS AND DESIGN

William R. Micks

Aero-Astronautics Department
The RAND Corporation

Introduction

We have all heard a great deal about the need for increased interaction between materials people and design people, and it has often been said that what is really needed is "better communication" between materials people and designers. However, it has not always been clear just what this better communication should consist of, or how it would be accomplished.

What I will try to do here is to give some possible answers to this question by describing a few of the primary functions that interaction between the two fields might perform, and to indicate some possible mechanisms for helping to accomplish this. And let me hasten to add that the problem is by no means solved; there is still a great deal yet to be learned.

To begin, I do not conceive of the subject of design as being separate from the subject of materials, but rather as an extension of the same subject at a different level of abstraction. You could not take materials out of design any more than you could take the gold out of a solid gold ring.

Both the materials specialist and the designer work with materials, but with different sets of ground rules and objectives. In one sense, the designer's function regarding materials might be thought of as managerial, where he is attempting to manage the materials in such a way as to achieve a certain overall objective. To do this he needs both information and substance from the materials area — information in the form of materials characteristics and behavior, and substance in the form of the materials themselves. However, there are certain contributions he himself must make to the process of bringing the information and the materials into existence, and this is what I will concentrate on in this discussion.

The Problem of Developing Materials Information for the Designer

Let us consider first the interaction between the materials and design areas on the subject of obtaining materials information for use by the designer. This is an area that is important to technological accomplishment and one on which a great deal of time and money is expended.

Since the designer is the user of the information, it is of course up to him to say what information he needs. However, those of you who have had experience in asking the designer what he needs have undoubtedly observed that in those cases where he is able to be specific, he frequently requests a great deal more information than can be reasonably furnished.

Because it costs money and man-hours to get experimental information, there has to be a balance between what one wants and what one is able or willing to pay. If we look

back for a moment at the analogy of the designer as a manager of materials, we could say that as part of his managerial responsibility he should consider carefully the expenditures that inevitably are associated with the acquisition of the information he requests.

We have to recognize that there are uncertainties that sometimes prevent the designer from knowing exactly what information to ask for. On the other hand, however, it is incumbent upon the designer to restrain himself from requesting everything for which he thinks there might conceivably arise a need. This is invariably too much.

Many of you undoubtedly are familiar with past attempts on the part of certain committee groups, representing the materials research community, to determine from structural designers what information was needed on the newer alloys that were then under development.

In one of these exercises, because the variables of temperature and time were involved in addition to the usual strength parameters, the list of "properties" that were requested by the structural design community was of such a magnitude that it was out of the question. There were not enough people or dollars to carry out the program, even if it had been thought desirable.

Undoubtedly one of the reasons for the magnitude of this particular list was that the designers were not sure at this time exactly which information they would eventually need for the final design. However, I think another major factor behind the tendency to ask for too much too soon is the failure to distinguish between the information required for exploratory or advanced design and the information required for detail design of hardware. This also raises a point concerning this hypothetical "designer" we talk about. It must be recognized that he is not one person with a single function, but rather is several people with several different functions in the design spectrum.

Exploratory design studies are continually being conducted in order to develop and evaluate new design concepts. These studies must of course use materials, which in many cases are new or projected materials; in order to design with a material, certain information must be obtained for design use.

However, the amount of materials information required for an exploratory design is much less than that required for a detail hardware design. And yet it seems to me that the mistake is often made of asking for detail design information on laboratory materials. Of course, even if it were possible to obtain this information it would not be useful for detail design because detail hardware design must in nearly all cases be based on production materials — not laboratory materials.

When the materials people are faced with, what to them appears to be an impossibly large request, they must pare it down somehow, and by this process they take on the function of deciding which parts of the total request are most important to the designer. Of course this is not a desirable situation. I am sure we would all agree that this function is the responsibility of the designer rather than the materials specialist.

What can be done to improve this situation? First, the materials people responsible for materials research planning should recognize that all designers do not wear the same color hats, and that the kind of information requested by a designer will likely be influenced by his particular area of the design spectrum. The list of required properties a detail designer would submit might be quite different from that submitted by a designer working on advanced design.

So we should try to make sure that the design inputs to the formulation of each kind of materials research program comes from the appropriate design area. Further, when the designer requests materials information we should try to make certain that the final program decided upon accurately reflects his real needs. In this later regard, I do not see any substitute for the designer and the materials specialist sitting down together and discussing what is needed and what it is to be used for.

Need for New Materials

Next we might look at the question of the designer's needs and desires (I hesitate to use the word "requirements") for new and improved materials and at the question of how the designer identifies these needs and communicates them to the materials community.

Guidance from the design area on this subject is usually somewhat more vague than on the subject of materials information; valid conclusions are harder to come by, and the uncertainties are greater, both in the full identification of needs and in the probability of satisfying the needs. Obtaining test information on materials is a fairly straightforward process, and one in which results are pretty well assured. However, you cannot be certain that the time and money expended in materials research will necessarily yield the material you would like to have.

There are two primary dimensions to the guidance needed here from the designer: first, what does he need, and second, how important is the need? It seems to me that we do quite well on the first of these and not nearly so well on the second.

I think the designers do pretty well on identifying future materials needs and problems; relatively few of these are missed for very long. The place where improvement is needed is the area of determining relative values or importance among the various needs.

It is seldom that one sees recommendations that call for less research, or cancellation of research in some particular area. I think nearly all the recommendations I have seen call for new research or for an increased level of effort in some area.

However, since the materials research manager has a finite budget and finite man-power resources, he must make the decision as to which research programs to implement, and at what relative levels of effort. (And of course this is not a decision he makes once and for all, but he must be continually reviewing and adjusting the programs.) This boils down to the fact that some research programs are implemented and some are not. Now we come to the question of the role that information from the design area could and should play in this decision process.

Role of Generalized or Parametric Design Studies

One of the most important resources the designer has for generating information for materials research guidance is the properly-structured generalized design study, and I would like now to discuss some aspects of its use. Because there are several different kinds of generalized studies, we will illustrate the type we mean by use of a simplified example.

By use of parametric or generalized design techniques, we could, for example, design a generic family of glide-rockets and we could determine the total vehicle weights associated with various combinations of payload and range, as illustrated in figure 1.

It is important to keep in mind that the vehicle, corresponding to any point on any of the lines of figure 1, has been optimized with respect to the design variables. The lines represent families of optimized vehicles. This is quite different from the optimization of a single vehicle for a specified mission.

One of the important parameters in our glide-rocket study is the maximum-allowable temperature of the leading-edge structure. If we want to study separately the problem of leading-edge materials, we can design a family of glide-rockets for a spectrum of (maximum) leading-edge temperatures, and thus isolate the effect of this parameter. This can give us information about the following:

1. What are the temperature-time ranges associated with this vehicle and what are the corresponding materials of interest?
2. How sensitive is the vehicle capability to the temperature capability of the leading-edge material?
3. How much must the material capability be improved (over current capability) in order to achieve a significant improvement in vehicle performance or efficiency?

By performing a similar exercise for various other important vehicle components, we can add a fourth item to the list:

4. In what areas is the capability of the vehicle most sensitive to changes in materials capability?

Each of the four items above has information of value to the question of planning materials research. If properly structured to answer these four questions, each vehicle design study that is carried out can furnish information not only about the feasibility and capability of the particular vehicle in question but also can furnish information of great value to the research function.

Taking the items in reverse order, Item 4 obviously helps to locate the areas where an improvement in materials will give the largest payoff. This is certainly relevant to the question raised previously concerning relative importance.

Item 3 is useful in setting minimum research goals, by showing what must be accomplished in materials research in order to achieve a specified level of improvement in the end item; this also helps in deciding which research program to undertake.

Item 2 is a special case of Item 3, and the type of information in Item 1 also helps to focus the area of inquiry in materials research by showing what ranges of parameters are of interest.

An example of the way in which one of the tradeoffs might appear is shown in figure 2, which plots vehicle gross weight as a function of allowable leading-edge temperature. For example, this curve shows the region of greatest sensitivity and also the level of achievement beyond which increasing leading-edge temperatures have very little payoff.

Obviously we cannot base our whole materials research program on only a few studies of this type; we must have many of these and on a continuing basis. At the present time there are large numbers of advanced design studies being carried on, but unfortunately for the materials research planner, few if any, of these studies are structured to give the kind of information discussed above.

The reason that most advanced vehicle design studies do not now furnish this kind of information is that they are usually conducted with a different purpose in mind. They are generally asking the question "What is the best vehicle that can be designed to meet a specified set of performance requirements (assuming some level of the state of the art)?"

What happens here is that the system is designed and optimized for the specified performance or mission requirements. In a section called "Material Requirements" may be listed the materials capabilities required by this system. In essence, however, such a list is merely a restatement of the optimistic (called advanced state of the art) assumptions made in the study. I submit that this kind of information is of doubtful value in guiding materials research and development. Besides being misleadingly disguised as proper research goals, such a list of requirements may introduce an additional risk if the system performance depends critically on the achievement of these goals. This risk is that the more optimism we put into the assumptions, the greater the lead-time, the greater the uncertainty, and the greater the research and development costs we are likely to be automatically building into the system. These quantities should not be the result of assumptions concerning the state of the art—they should be the cause of these assumptions. Otherwise we have the cart before the horse.

The relationship of research goals to their corresponding cost, time, and uncertainty of attainment should be examined as carefully as possible; these quantities should be inputs into the decision process of what research to undertake and what state of the art to design a particular system for.

I am not saying that we shouldn't design advanced systems with advanced materials. We should conduct these design studies using a spectrum of materials capabilities (some of which are beyond the current state of the art). Then we have the basis for including, in our subsequent decisions relative to procurement of a particular vehicle, a proper consideration of the factors of lead-time, research and development costs, and the effects of achieving less than the full research goals. We can then see what the tradeoffs are and make the decisions accordingly. And consequently, by the way in which we design the vehicle, we can buy some insurance against the uncertainties of achieving certain research goals.

Overall Interactions

In conclusion I would like to show you a chart (figure 3), admittedly over-simplified, that illustrates some of the functions of the materials/design interplay that have been mentioned and their relationships to one another. This chart has been drawn to show particularly the role of generalized design studies in the materials/design interaction.

The contributions of the design area are depicted here in the blocks beginning with the advanced design studies and proceeding to the formulation of candidate research programs, which should be a joint function as indicated. The materials functions begin at this same block and proceed to the function of materials testing for advanced design information, which is also a joint function.

Although this chart separates the area of design function and materials function, this separation applies only to the question of primary responsibility for the various functions, not to the activities involved in the functions. For example, the design study is shown here as a design function, yet it certainly should have materials specialists on the design team. Likewise, there should be people from both areas participating in each of the activities shown in the various blocks.

I think this chart is self-explanatory but there are two things I want to point out. One is the separation of testing for advanced design and testing for detail design that was discussed earlier.

The other thing I want to call attention to is the step going from the design studies to the formulation of candidate research programs for the materials research planner to consider. At the present time this is one of our major areas of inexperience. I think two things should be done to improve our handling of this area and to exploit an untapped potential that exists here.

First, there should be a few study activities conducted whose primary objective is to develop a methodology of structuring design studies to give the desired outputs discussed earlier and to explore and develop processes of converting these outputs into complete outlines of corresponding research programs. (The Air Force has recently given some attention to this subject and I would certainly encourage further action in this area.)

Second, when the methodology above has been developed to a point where it can be helpful, the Air Force should require wherever possible that funded design studies include, as an integral part of the study, the type of input-output relations discussed above that furnish the information needed for materials research planning.

I think this latter requirement would have a two-fold payoff: 1) it would furnish much-needed information for materials research, and 2) the increased attention to materials vs vehicle performance tradeoffs would result in a better vehicle design than one would obtain otherwise.

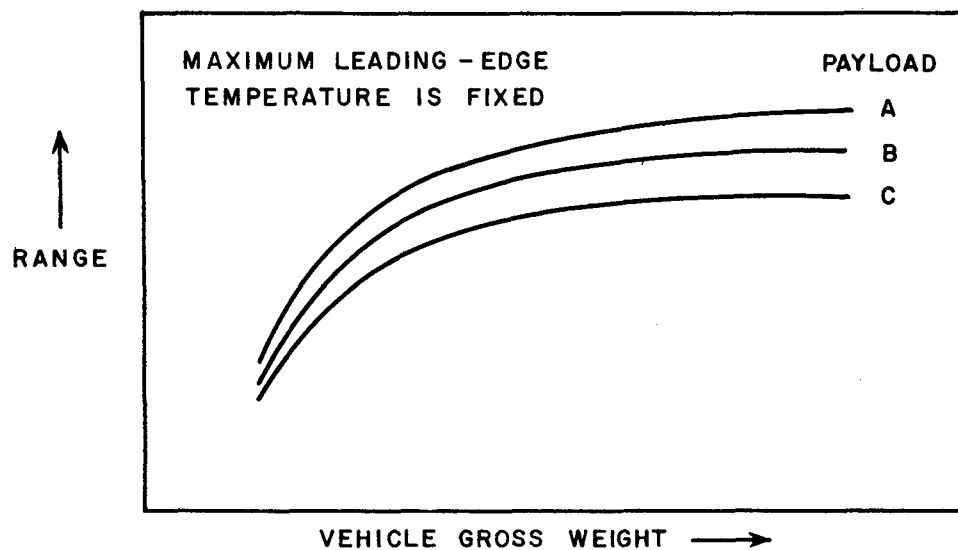


Fig. 1 — Generalized glide — rocket design

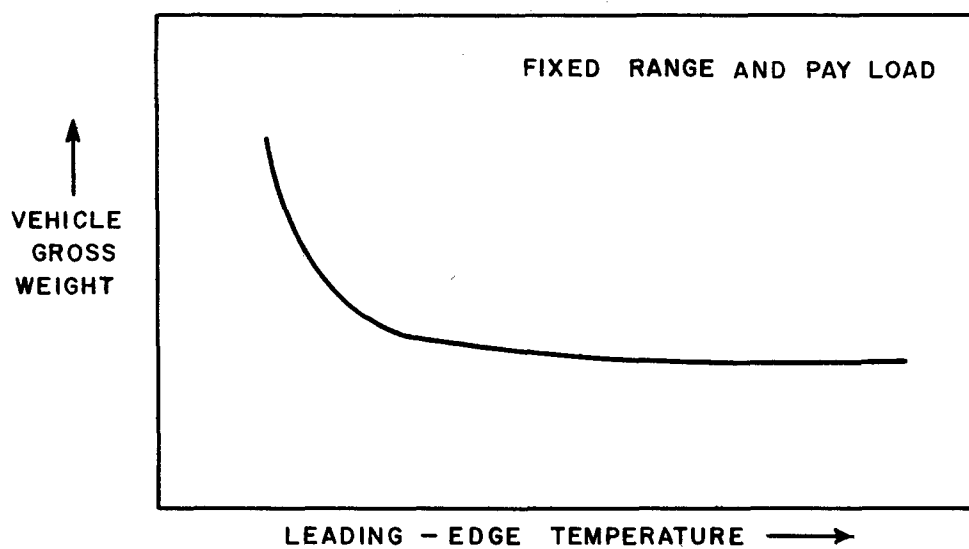


Fig. 2 — Influence of allowable leading — edge temperature on glide — rocket weight

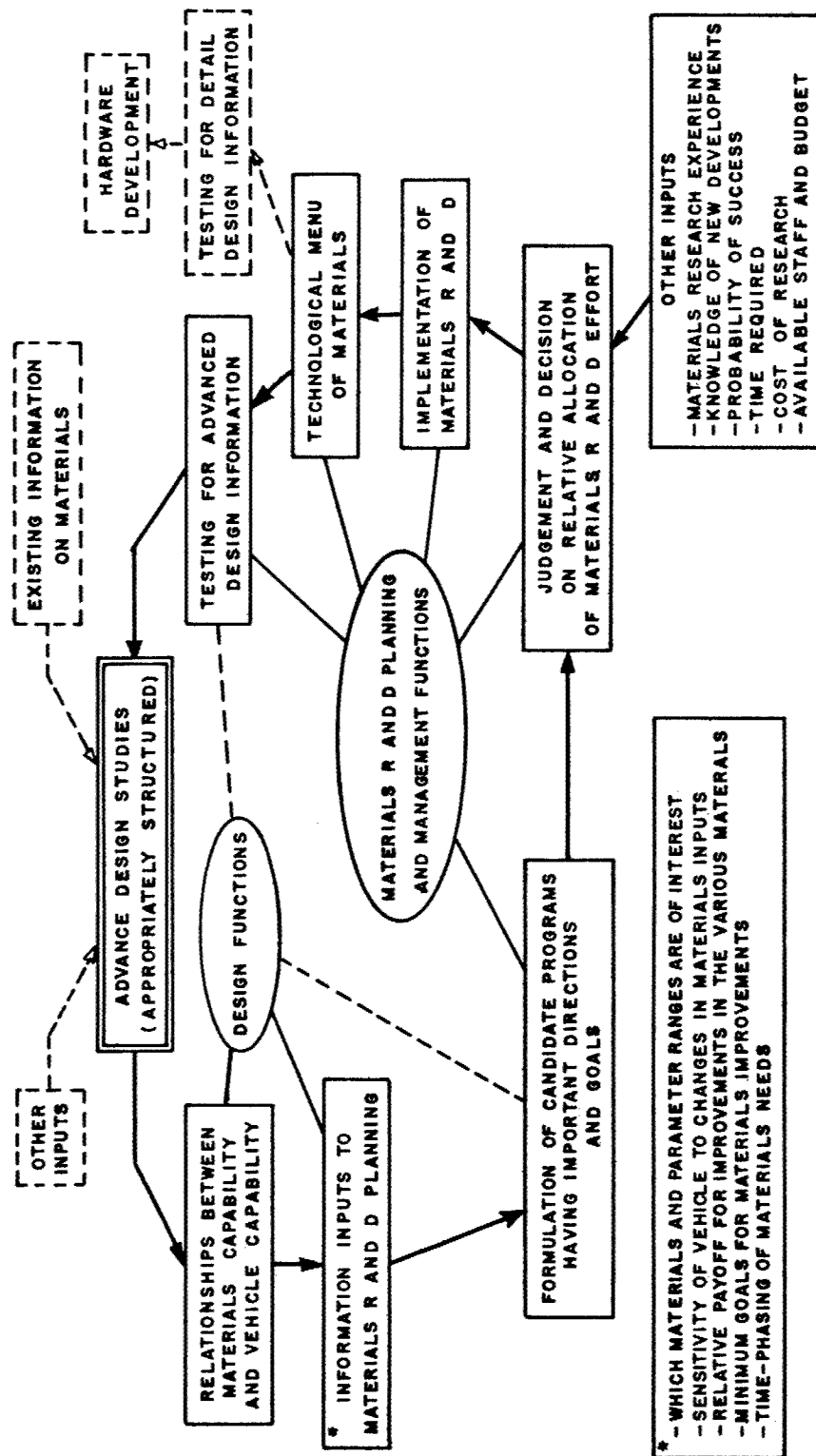


Fig 3 — Role of advanced design studies in the design / materials interaction

WELDING AND BRAZING

Chairman

Mr. R. Bowman

Speaker

Mr. J. Gow

Panel Members

Mr. B. Price

Mr. P. L. Hendricks

WELDING AND BRAZING SPACE AGE METALS

R. Bowman

Directorate of Materials and Processes, ASD

Introduction

To achieve the performance desired in future aircraft, missiles and spacecraft, it will be necessary to use structural materials and alloys which have the highest possible strength to weight ratio at the temperatures of operation. These materials will include newly developed metals or alloys, such as, beryllium, titanium, high strength steels, nickel-base alloys and the refractory metals, columbium, molybdenum, tantalum and tungsten. The development of these alloys requires a corresponding development in joining methods which will provide joints with properties that match as closely as possible those of the parent metal. The efficient utilization of an alloy in a structure or component will often require that the joints be made by welding or brazing. The new alloys have presented more difficult problems in welding and brazing and have made it desirable also to investigate new and unconventional joining methods, such as, ultrasonic, electron beam and explosive welding. The use of sandwich construction, likewise, has created additional requirements for new brazing methods and materials. A continuing research and development effort is required to solve these problems and to establish the optimum welding and brazing procedures for the construction and repair of aerospace equipment.

A discussion of some of the major problems was presented at the Materials Symposium held in Dallas, Texas, 10 July 1958. Since that date new developments have been made and new problems have been encountered which make this discussion appropriate.

Applicable Processes

Before proceeding with the discussion of the problems involved in the joining of specific alloys, it is desirable to review briefly the welding and brazing processes which are used frequently in the aerospace industry, and to mention recent developments in joining that may have application in the aerospace industry.

Welding Processes

Manual gas welding and metal arc welding were the first fusion welding processes to be used by the aerospace industry. These processes are still in current use but they have been replaced to a great extent by the inert-gas metal-arc welding process. The latter process when compared with gas and metal-arc welding has an important advantage: there is no reaction between the inert gas and the weld metal. In gas or metal-arc welding, the gas or slag reacts with the molten pool of the active metals. This characteristic restricts the use of these processes to welding of the less reactive metals, iron, nickel, and aluminum. The inert-gas shield permits arc welding of all the metals and alloys, including the reactive metals titanium, columbium, molybdenum, tantalum and tungsten. Arc spot welding, a modification of the inert-gas metal-arc welding, is being used in many more applications. This process allows spot welds to be made when the joint is accessible from only one side. The inert-gas metal-arc process is readily adaptable to automatic welding in which all variables are closely controlled. Elaborate devices have been developed for controlling the important variables associated with the process.

Electron beam welding is one of the more recent processes of great interest. This process consists of accelerating electrons to a high velocity in a vacuum and allowing them to strike the joint where a weld is desired. The electron beam can be focused within a very small diameter spot which produces a weld with deep penetration and a very narrow fusion zone. The high vacuum required for the electron beam reduces contamination in the weld to a low level. The major disadvantage of this process in its present state of development is that the part to be welded must be completely enclosed in the vacuum chamber. Possible methods of overcoming this disadvantage are under investigation in programs supported by the Air Force. The electron beam process will be suitable for welding in space environments in the future. A high vacuum exists in outer space which eliminates the need for a chamber to enclose the electron gun and the parts to be welded.

The plasma-jet has been proposed as a new welding method, but some of the recent investigations indicate that this method is more suitable for metal spraying or surfacing on parts requiring a minimum of penetration into the parent metal.

Resistance spot and seam welding has been used successfully in the aerospace industry for joining all of the weldable alloys. The recent trend toward the use of refractory alloys will present a serious problem of avoiding tip pickup. Possible solutions to this problem include the use of projections to concentrate the current at the interface, while a flat tip is used at the outer surface to distribute the welding current over a larger area where the tip is in contact with the sheet. Other resistance welding processes of interest to industry include flash welding for making butt joints in sheet, bar stock, tubing and similar joints and the high frequency welding which is used in the manufacture of tubing.

There has been an interest in the more recent processes which probably involve solid state bonding. These processes include ultrasonic welding, friction welding, diffusion bonding, and explosive welding. Ultrasonic welding has been successful in joining aluminum to aluminum and also dissimilar metals such as aluminum to copper or aluminum to steel. Further development is required to make this process suitable for joining the high strength alloys or the refractory metals. Programs have been initiated with the objective of developing ultrasonic equipment with a greater power output which may extend the range of materials that can be welded. Friction welding appears suitable for making butt welds in tubing similar to those produced by flash welding. More data on friction welding is required to determine the advantage of this process. Diffusion bonding has been used in the manufacture of fuel elements and has promise as a method of joining difficult combinations of alloys when other joining methods are not adequate.

Explosive welding is a new process which was discovered accidentally in explosive forming. A limited investigation completed recently indicates that small plates of similar and dissimilar alloys can be bonded with explosives. Sufficient data is unavailable on this process to determine useful applications. Possible applications may include bonding dissimilar combinations or welding at remote locations; explosive welding may be useful in the assembly of future space stations.

Brazing Processes

Many components in the aerospace industry are fabricated by various brazing processes. Brazing is used in the fabrication of liquid rocket engines, heat exchangers, jet engine components, hydraulic lines, fittings and similar parts. Brazing of these components require some development effort to obtain the optimum procedures, brazing filler metals, and atmospheres. The major effort however, in recent years has been aimed at developing techniques and brazing alloys which will be suitable for the fabrication of brazed

sandwich panels. The brazed honeycomb sandwich panel is an ideal structure but presents difficult problems in fabrication.

Sandwich Structures

Progress has been made toward the solution of problems encountered in the fabrication of brazed sandwich panels. This progress is the result of extensive research and development programs supported by the Air Force and the aerospace industry. A number of different brazing methods have been investigated in an effort to reduce the time required for brazing. The methods include the use of the conventional furnace, radiant furnace, electric blanket and the quartz lamp radiant heating. The Air Force has recently sponsored projects on the development of radiant furnace and quartz lamp radiant brazing methods. Additional work with the electric blanket method is included in the program on the development of the B-70 airplane. While all methods may have some application on future aircraft, the electric blanket method or modifications of this method appears to have the greatest utility. The major part of the PH 15-7 Mo steel panels for the B-70 airplane have been brazed with the electric blanket method. This method has a number of advantages over furnace brazing: (1) the time for brazing is shorter (2) the amount of handling can be reduced since the panel can be brazed and heat-treated in the same fixture (3) distortion during brazing and heat treatment can be controlled with less difficulty as the panel is held in the jig throughout the cycle. The quartz lamp radiant heating also has promise as a method of reducing the time required for brazing. This method has successfully produced panels of PH 15-7 Mo steel with flat, single curvature and complex curvature surfaces. Another form of radiant heating which uses a Globar furnace was successful in brazing honeycomb panels, 12" x 12" x 1/4", made of both Inconel 702 and Haynes No. 25 alloy.

Progress has been made in controlling the flow of the brazing alloys in PH 15-7 Mo steel sandwich panels. In all brazing methods, contamination of the surfaces is avoided by carefully cleaning the parts and then placing the assembly in an envelope which is filled with a high purity inert gas. A small amount of lithium, about 0.2 percent is added to the brazing alloy to improve wetting by removing residual surface oxides. The composition of the brazing alloy is adjusted so that its flow temperature will be compatible with the heat-treatment cycle. A silver base alloy containing 7 percent copper and 0.2 percent lithium is frequently used for the attachment of the cover sheet to the core. Modifications of this alloy include the addition of palladium and indium which lower the thermal conductivity of the alloy or the use of the alloy in a nickel sponge to reduce the drainage of filler metal to low places. The silver-copper-lithium alloy has produced brazed joints with satisfactory fillets and soundness for the attachment of the cover sheet to the core in PH 15-7 Mo steel panels. This alloy, however, has not been satisfactory for the edge attachments on the panel because of the formation of voids at the interfaces of the lap joint. The major cause of the voids is probably the high vapor pressure of the lithium addition. The voids have been reduced by using another silver alloy containing 32.5 percent copper and 5 percent nickel.

In recent years some of the effort on the development of brazed sandwich panels has been shifted from PH 15-7 Mo stainless steel to the super alloys and the refractory metals. The work on sandwich panels of super alloys, and refractory metals is part of the effort to develop structures that will withstand the high temperatures of re-entry into the atmosphere. In a program sponsored by the Air Force, procedures were developed for brazing panels of both Inconel 702 and Haynes 25 alloys. The brazing of similar panels of molybdenum - 0.5 percent titanium alloy in this program was not successful.

One of the major problems in the brazing of these materials is the development of brazing alloys and procedures which will reduce erosion of the thin sheet and embrittlement of the alloy. A nickel base alloy containing 19 percent Cr and 10 percent Si was adequate for the Inconel 702 and Haynes 25 alloy panels but no satisfactory alloy was found for the molybdenum - 0.5 percent titanium alloy panels which were suitable for temperatures above 2000°F. This investigation included nickel-base and cobalt-base brazing alloys. Additional development work is desirable to obtain the optimum procedures and filler metals for brazing the super alloys and the refractory metals. The current effort in this area includes an investigation to determine the feasibility of using volatile elements such as indium, in brazing alloys to lower the flow temperature. After brazing, the element is volatilized to raise the remelt temperature. Other work covers the development of brazing alloys for columbium and tungsten as will be described later. Consideration is also being given to the extension of the work on radiant brazing methods to include refractory metals.

Joining Problems in Aerospace Metals

The problems encountered in joining specific alloy groups will now be discussed. The alloy groups will include beryllium, titanium, high strength steels, precipitation hardening stainless, high temperature alloys and the refractory metals. Magnesium and aluminum will be omitted since the Air Force has no current development projects in this area.

Beryllium

The problem of joining beryllium was mentioned briefly in the previous materials symposium. It was stated that a program had been initiated to investigate possible methods of joining beryllium along with other problems associated with the application of beryllium in useful structures and components. The program sponsored by the Air Force includes the conventional welding and brazing processes.

Prevention of cracks at fusion welds is a major problem. One possible cause of cracking is the low ductility of beryllium at room temperature combined with the high thermal stresses produced in welding. When the product of the modulus of elasticity and the coefficient of expansion is used as an indication of the ease in which the thermal stresses can be produced, beryllium occupies an unfavorable position in a comparison with other metals. When the common metals are arranged in order of increasing product, table 1, it is noted that beryllium has the highest product while columbium has the lowest. Beryllium is also among the metals having the lowest ductility. The high product combined with the low ductility indicates that beryllium must be fabricated with procedures that produce a minimum of thermal stresses.

Another possible cause of the cracks is hot tearing which is due to the formation of low melting point constituents in the grain boundaries. This conclusion is supported by the results obtained in the present program. It has been shown that the susceptibility to hot tearing in beryllium fusion welds is increased by increasing the aluminum content in and above the range found in commercially pure beryllium, up to several percent aluminum. Other residual impurities in beryllium may contribute to cracking in a different manner. As an example, in beryllium, iron forms intermetallics which have lattices different from that of beryllium. The difference in lattice structure may produce stresses in beryllium and increase the tendency to crack at the welds. The major impurity, BeO, in beryllium appears to have no effect on cracking when present in amounts less than 2 percent. Another condition which probably increases the cracking tendency is the large grain size in the fusion welds.

Progress has been made in the development of procedures for fusion welding of beryllium. The inert-gas arc-welding process has produced crack free welds in laboratory specimens with sheet thicknesses under 1/4 inch. Small components made of beryllium have been welded successfully. Cracks are minimized by avoiding thermal shocks and by using low welding currents and slow welding speeds. More refinements in procedures are required for welds in thick plates or large structures where the joint is under more restraint. Other problems in fusion welding are: mechanical properties of the weld are lower than those of the parent metal, satisfactory penetration is difficult to obtain because of the high heat conductivity of beryllium combined with the requirement for low welding current, and excessive grain growth is difficult to avoid in the weld and heat affected zones. Solutions to these problems must be found to extend the use of fusion welding. Techniques such as roll planishing to improve the strength are now being attempted with some success. Other fusion welding processes such as electron beam welding may provide additional improvement.

Ultrasonic welding of beryllium sheet ranging in thickness from 0.010 to 0.013 inch is under investigation. Sound welds have been made without an accompanying increase in the grain size in the weld area. The cracking tendency at the weld is reduced by using short periods of power application, usually less than 0.5 second. The short time interval requires an increase in the power level to make the weld and limits the maximum thickness that can be welded with the available equipment. To reduce the power requirements, an investigation was initiated to determine the effects of welding through foil interleaves of various metals such as aluminum, zirconium and gold. The technique of using foil interleaves shows definite promise but more data are required to make a complete analysis.

An investigation of resistance butt welding and spot welding has been initiated. Some resistance butt welds were made in 5/8-inch diameter beryllium rod but additional tests are required to evaluate this process. Preliminary results of tests of spot welds in 0.040-inch sheet indicate that both preheating and postheating are required to eliminate cracking. The results are encouraging but more tests are needed for making definite conclusions.

Results reported by several investigators indicate that beryllium can be joined by brazing with silver base or aluminum base alloys. To date, brazing is considered as the most reliable method of joining beryllium. Brazing alloys have been developed which give a satisfactory bond with approximately 60 percent of base metal strength at room temperature. The program on brazing beryllium will be continued and the effort will be directed to the development of improved brazing alloys and procedures.

Titanium

Titanium and titanium alloys are joined by inert-gas-shielded metal-arc welding and by spot, seam, flash, and pressure welding. For arc welding, procedures have been developed which avoid contamination of the welds by oxygen and nitrogen from the air. These procedures include the use of large gas nozzles, trailing shields and backing bars with means for introducing the inert gas on the underside of the weld. Also, chambers filled with an inert gas are in use to provide shielding for parts that cannot be adequately shielded by other methods. The major problem is now the brittleness of fusion welds in the higher strength titanium alloys. The Air Force sponsored a program aimed at the development of more weldable medium strength titanium alloys having a yield strength of 130,000 psi but no alloys were obtained which have better weldability than current commercial alloys. The current alloys that are frequently used in welded structures include Ti-5Al-2.5Sn, Ti-6Al-4V and Ti-13V-11Cr-3Al,

representing respectively the alpha, alpha-beta and beta alloys. Although successful weldments have been made with these alloys, additional research and development is required to obtain the optimum properties in the welded joints.

Some progress has been made in the development of procedures and brazing alloys for the fabrication of brazed titanium sandwich panels. The procedures are similar to those used for stainless steel sandwich panels. Some modifications are required to make the brazing cycle compatible with the heat treatment cycle required for the titanium alloy. The brazing is accomplished near the solution temperature as part of the heat-treating operation. This requires that the brazing alloy have a flow point from approximately 1450°F to 1600°F. The most suitable brazing alloys at this date are silver base alloys containing 5 percent or 12.5 percent aluminum. Silver-lithium alloys have been investigated but the corrosion resistance of these alloys was found unsatisfactory. For a number of applications it is desirable to braze the titanium alloy at the aging temperature, usually below 1100°F. At this temperature, it has been difficult to obtain satisfactory flow of a brazing alloy on titanium. The present programs sponsored by the Air Force include the development of alloys for brazing titanium during the aging cycle.

High Strength Steels

The welding of high strength steels has been a subject of major interest to the aircraft and missile industry. Welding was first used by the aerospace industry in the fabrication of airframes, landing gears, engine mounts and similar components made of SAE 4130, 4140, or 4340 steels. The major development effort in recent years has shifted from welding these components to the welding of missile cases. New steels, 300M, X-200, D6A, H-11, and others have been added to list of aircraft steels. Also, the steels are heat treated to higher strengths. Yield strengths of 230,000 psi and higher are now being considered for steels in missile cases. The use of welding is essential in the fabrication of missile cases of high strength steels. A major effort has been directed to the development of filler wires and welding procedures which will produce welds of the desired strength, ductility and soundness. The inert-gas-shielded arc welding is the most frequently used process. Other processes, metal arc, submerged arc and resistance welding have also been used but less extensively. Development of filler wires which produce welds of the desired strength has been achieved. Filler wire of a composition similar to the parent metal is usually used so that the weld will respond to heat treatment in the same manner as the parent metal. The carbon content of the filler wire is often below that of the parent metal to reduce the cracking tendency and to improve the ductility. With this type of filler wire it is not difficult to obtain welds with strengths approaching that of the parent metal but welds with the desired ductility and soundness are not always obtained. Because of the difficulty involved in obtaining welds with the required soundness and ductility some fabricators have avoided the use of longitudinal welds and have used only girth welds on the missile cases. Progress has been made in improving the ductility and soundness of the welds.

The reduction of hot cracking has improved the soundness of the welds. Results obtained in recent programs show that sulfur and phosphorus in amounts allowed by commercial specifications for steels can contribute to hot cracking. The results of a typical study are presented in figure 1 which shows the detrimental effects of sulfur on the hot ductility of SAE 4340 weld metal. Lowering the sulfur content from 0.031 to 0.012 percent increases the temperature at which there is a sharp drop in hot ductility. Similar results have been obtained for the effects of phosphorus. Based on these results many specifications for filler wire now require very low sulfur and phosphorus. Further progress in avoiding weld cracks has been made by using the optimum temperature for preheating and

post-heating. The isothermal transformation diagrams are useful in the determination of the optimum preheating and postheating procedures. An analysis of these diagrams for SAE 4340 and 300M steels (figure 2) indicates an optimum preheating and postheating temperature of 600°F. Temperatures above 600°F require longer times for the austenite to bainite transformation. At temperatures below 575°F martensite forms. Longitudinal bend tests of welds made with a 600°F preheat and postheat, show much better ductility than similar tests of welds made with higher or lower preheat and postheat temperatures. Good fixtures and proper cleaning of the filler wire and parent metal are also helpful in the prevention of cracks and porosity in the welds. Another essential part of the procedures is to avoid contact between the hot weld metal and the copper backing bars. Cracks can be caused by rapid cooling when the hot weld metal contacts the copper bars.

These procedures are effective in improving the weld soundness but do not always produce the desired ductility in the weld metal. Procedures which will improve the ductility of welds are of major interest. As mentioned previously the use of filler wires with lower carbon content is effective in improving the ductility. Additional improvement is obtained by heat treatments which refine the austenite grain size in the weld metal and heat affected zones. A number of research laboratories have proposed investigations of various possible methods of improving the ductility and soundness of welds. These methods include magnetic stirring of molten pool, pulsing of the welding current and the application of vibrations to the molten pool. An existing program includes the development of improved filler wires and procedures for welding the hot work die steels. Other possible programs of interest in the welding of missile cases are the development of more sensitive methods of nondestructive inspection. Many failures in rocket cases started at weld flaws which were not detected in the nondestructive inspection.

Precipitation Hardening Stainless Steels

The manufacturers and users of these steels have developed filler wires and welding procedures which produce welds with better ductility without a serious drop in strength. An important part of the procedures is the adjustment of the chemical composition of the weld metal so that the required amount of delta ferrite is formed in the weld metal. A small amount of delta ferrite, about 15 percent, is required in PH 15-7 Mo weld metal to obtain the optimum physical properties when the part is heat treated after welding. The inert-gas tungsten-arc welding process is used most widely on these steels. This process provides efficient protection of all the alloying elements and allows close control of the chemical composition of the weld metal. The solution to another problem is required before the precipitation hardening stainless steels can be used efficiently in aircraft structures of the future. One proposed design for these structures requires the assembly of brazed honeycomb panels by welding the edge attachments, figure 3. The joints will be used in the as welded condition. The control of warpage and residual stresses at the welded joints may be a serious problem in the assembly of the large rigid structures. The residual stresses in these structures may contribute to brittle failures or they may increase the susceptibility of the alloy to stress corrosion cracking. Residual stresses have been shown to be a contributing factor to brittle failures in large welded structures of low carbon steels.

High Temperature Alloys

The problem of major interest in welding these alloys is cracking at the welds in the age hardenable alloys, such as, A286, Inconel X and Rene 41. These alloys have additions of titanium and aluminum to obtain higher strengths by heat treatment which includes a solution treatment at a relatively high temperature, usually from 1650°F to 2200°F,

followed by an aging treatment usually between 1200°F to 1600°F. The physical properties of these alloys are adequate for a large number of applications, but the additions of aluminum and titanium tend to lower their weldability. Progress has been made for production welding of these alloys and in understanding their behavior from a metallurgical standpoint. However, welding problems still arise in production welding of these alloys, and more development of the process is required. Sound fusion welds can usually be made in the high nickel alloys, Inconel X and Rene 41, when they are in the solution heat-treated condition. With the alloy in this condition, cracking during or immediately after welding does not appear to be the major problem. However, during the subsequent heat treatment, they have a serious tendency toward strain age cracking when the part is heated through the aging period temperature range. In the A286 alloy, most of the cracking occurs during or immediately after welding. It appears that there is a hot short range just below the melting point of the alloy. The Air Force is sponsoring a program to obtain more information on the mechanism of cracking and to develop procedures which will reduce the tendency to cracking in these alloys.

Refractory Metals

Molybdenum was the first metal of this group to be considered for use by the aircraft industry. Initially, molybdenum and its alloys were investigated as a material for use in ramjet and turbojet engines. More recently, molybdenum alloys are being considered for the construction of hot structures on re-entry vehicles. All of these applications require that molybdenum be joined by some method, preferably by welding or brazing. With the shielded inert gas arc welding processes, sound welds can be made in molybdenum by exercising a high degree of process control but the ductility of the weld at room temperature is usually less than that desired for airframe structures or engine components and the weldments are very notch sensitive. The ductility is lowered by the recrystallization in the fusion and heat affected zones. A similar embrittlement will occur in brazing when molybdenum is heated above the recrystallization temperature. Extensive research and development programs have produced data which show that minute quantities of oxygen, nitrogen and carbon contribute to the embrittlement. Thus, the major effort in the welding of molybdenum has been directed toward the elimination of these impurities from both the weld and the parent metal which has been accomplished by the use of ultra-high-purity molybdenum as the base metal, and by welding in dry boxes which have been vacuum-purged and filled with an inert gas of high purity. Other methods of improving the ductility of molybdenum welds include postweld heat treatments, cold working of welds, high welding speeds and stressing the weld at elevated temperatures. Even with these methods, the desired ductility in molybdenum fusion welds is difficult to obtain. More recent developments include the use of the Mo-50 percent Re alloy as the weld metal to lower the ductile to brittle transition temperature of the weld bead and the use of electron beam welding to reduce the contamination of the weld and also the width of the heat affected zone.

The Air Force is sponsoring a program on the electron beam welding of molybdenum and tungsten. These developments may provide additional improvement in the ductility of molybdenum fusion welds. Low ductility is also obtained in resistance spot welds joining molybdenum. Another problem in spot welding molybdenum is sticking of the electrodes. Because of these problems, the Air Force sponsored an investigation of ultrasonic welding which included the joining of molybdenum. Sticking of the tip to molybdenum was also a problem in ultrasonic welding. A more serious problem was the cracking at the edges of the welds, figure 4. To obtain an ultrasonic weld, it is necessary to apply the vibrations of the tip in a plane parallel to the sheet surface. This requirement creates the problem of transferring the energy from the tip to sheet surface, then through the sheet thickness to the interfaces where the weld is desired. In soft alloys, similar to aluminum, sufficient

energy can be transferred to make a weld without cracking, but in the hard metals, such as molybdenum, the transfer of the required energy becomes more difficult. Investigators report varying degrees of success in ultrasonic welding of molybdenum. Variations in welding equipment and procedures may improve ultrasonic welds in molybdenum but the problem of transferring energy to the interface will certainly limit the practical use of this process to the thinner sheets of molybdenum.

Since the discovery of large deposits of columbium ore, this metal and its alloys have been investigated for possible use in structures and components in which a higher operating temperature is desired. The current investigations include welding and brazing along with other investigations connected with the application of columbium. Tungsten arc welds with good ductility can be made in unalloyed columbium if reasonable care is exercised to avoid atmospheric contamination. Nitrogen and oxygen can embrittle columbium but its tolerance for these impurities is much greater than in the case of molybdenum. Although most of the wrought form higher strength columbium alloys are ductile at or below room temperature, the welding operation produces a zone of fused metal and a recrystallized heat-affected-zone of greatly reduced ductility. A precipitation process may contribute to the embrittlement. The addition of alloying elements to columbium can raise the ductile to brittle transition temperature. Some elements, vanadium, tantalum, titanium, hafnium and zirconium can be added in fairly large amounts without raising the transition temperature. Small additions of other elements, such as tungsten, molybdenum and chromium cause a rapid rise in the transition temperature. Thus, the development of weldable columbium alloys requires a careful consideration of the effects of alloying elements on the ductility of the welds.

Additional problems that should be investigated include the effects of the interstitial elements on the physical properties and weldability of columbium alloys. Also welds in some of the commercial columbium alloys are reported to have low ductility. The Air Force has initiated a program to study the weldability of commercially available columbium alloys, FS 82, D 31 and F 48. The effects of various welding parameters including welding speeds, atmospheres, preheating and post heat treatments on the metallurgical and mechanical behavior of these alloys will be investigated.

Brazing is a subject of interest in the fabrication of structures from thin columbium sheets. Brazing alloys suitable for temperatures to 2500°F are usually desired for structures made of columbium alloys. Development of columbium brazing alloys is included in the current Air Force development programs. Brazing alloys under investigation include titanium, titanium-vanadium and binary alloys of columbium formed by additions of vanadium, titanium, zirconium and boron.

The welding characteristics of tantalum are similar to those of columbium. Tantalum can be welded with shielded inert gas arc welding, resistance welding and electron beam welding. The procedures are similar to those used in welding of molybdenum or columbium. The welds in pure tantalum have excellent ductility, however, because of its low strength to weight ratio, and because the development of tantalum base alloys was initiated only recently, it is of little interest in the aerospace industry.

Tungsten can be welded by the inert gas shielded arc processes. The procedures are similar to those used in the welding of molybdenum. The electron beam welding process can also be used. Sound welds can be made in tungsten but they are very brittle at room temperature. The problem of obtaining ductile welds is very difficult as the transition temperature of tungsten is approximately 600°F higher than that of molybdenum. The transition temperature of welded joints in tungsten is not appreciably higher than that of

the base metal. Programs are in progress on welding and brazing of tungsten. Specific areas of investigation in welding, cover the effects of interstitial content, tungsten arc, electron beam welding, and the use of tantalum as a filler wire. The brazing phase of the investigation will include the brazing of alloys suitable for service up to 3500°F. Binary alloys of tantalum, columbium and molybdenum which have additions of titanium, vanadium or other elements to lower the melting point will be investigated. The objective of this work is to gain a sound metallurgical insight into the physical metallurgy of joining tungsten by welding and brazing. The metallurgical reactions that occur during the joining process are to be evaluated so that procedures and filler metals can be developed for producing the best possible properties in the joints.

Summary

Major problems in welding and brazing aircraft and missile components have been reviewed and are indicated in table II. Progress has been made in welding beryllium but additional development is required to consistently make sound welds that are crack-free. Further improvements in the soundness and ductility of fusion welds in high strength steels and the high strength titanium alloys are desirable. The welding of brazed honeycomb panels to form an airframe structure is a challenge of major importance in the construction of Mach 3 aircraft. Cracking at the welds in the age hardenable high temperature alloys should receive additional attention. Welding of the refractory metals should also receive additional attention. The transition temperature of fusion welds in molybdenum is still too high for structural applications. New methods for joining molybdenum, such as diffusion bonding should be investigated. Additional work in the welding of columbium alloys is necessary to obtain satisfactory properties in the alloys of higher strength. Utilization of tantalum alloys in aerospace structures and components will require the development of weldable alloys of higher strength. Further refinements in welding techniques for joining tungsten are necessary to obtain sound welds consistently and to reduce the brittleness at room temperature. The brazing of all alloys mentioned in the preceding discussion should receive additional attention. Brazing alloys and techniques for the refractory metals are however, of special interest, while continuing research and development programs in welding and brazing must be continued to solve joining problems for the aerospace industry.

References

- (1) Mac Pherson, B. M. and Beaver, W. W., "Fusion Welding of Beryllium," WADD Technical Report 60-917.
- (2) Passmore, E. M., "Beryllium Joining, WADC Sponsored Program," WADC Technical Report 59-695.
- (3) Faulkner, G. E. and Voldrich, C. B., "The Welding of Titanium and Titanium Alloys," DMIC Report 122.
- (4) McAndrew, J. B. and Levinson, D. W., "Development of a Weldable Titanium-Base Alloy of Medium Strength," WADC Technical Report 58-173.
- (5) Rieppel, P. J., Monroe, R. E., Mishler, H. W., "Determination of the Causes of Weld-Metal Cracking in High Strength Steels and the Development of Heat-Treatable Low-Alloy-Steel Filler Wires for Use With the Inert-Gas-Shielded Arc-Welding Process," WADC Technical Report 59-531.
- (6) Lehrer, W. B. and Schwartzbart, H., "Development of Partially Volatile Brazing Filler Alloys for High Temperature Applications," WADC Technical Report 59-404.
- (7) Pattee, H. E. and Evans, R. M., "Brazing for High Temperature Service," DMIC Report 149.
- (8) Martin, D. C., Thompson, V. R., Vagi, J. J., "Welding of High-Strength Stainless Steels for Pressure Vessels," Report No. BMI-911.
- (9) Weisenberg, L. A. and Morris, R. J., "How to Fabricate Rene 41," Metal Progress, 70-74, November 1960.
- (10) Jacobson, M. I., Martin, D. C., and Voldrich, C. B., "Production of Sound Ductile Joints in Molybdenum," WADC Technical Report 53-401.
- (11) Platte, W. N., "Joining of Molybdenum," WADC Technical Report 54-17.
- (12) Begley, R. T., "Development of Niobium-Base Alloys," WADC Technical Report 57-344.
- (13) Weare, Antonevich, Monroe and Martin, "Research and Development of Procedures for Joining of Similar and Dissimilar Heat-Resisting Alloys by Ultrasonic Welding," WADC Technical Report 58-479.
- (14) Lewis, Antonevich, Monroe and Rieppel, "Fundamental Studies on the Mechanism of Ultrasonic Welding," WADD Technical Report 60-607.
- (15) Jones, J. B., Maropis, N., Thomas, J. G., Bancroft, D. , "Fundamentals of Ultrasonic Welding," Bureau of Naval Weapons Research Report No. 59-105.
- (16) Preston, O., "Feasibility Study of Plasma Welding of Refractory Metals," Final Report, Contract No. NOas 59-6234-C, Bureau of Naval Weapons.

TABLE I

PRODUCT OF THE MODULUS OF ELASTICITY AND THE COEFFICIENT OF
EXPANSION FOR SOME OF THE COMMON METALS

METAL	MODULUS OF ELASTICITY PSI	COEFFICIENT OF EXPANSION IN./°C	PRODUCT
COLUMBIUM	15×10^6	7×10^{-6}	105
TITANIUM	16.8×10^6	8.5×10^{-6}	143
MAGNESIUM	6.5×10^6	26×10^{-6}	169
TANTALUM	27×10^6	6.5×10^{-6}	175
TUNGSTEN	50×10^6	4.3×10^{-6}	215
CHROMIUM	36×10^6	6.2×10^{-6}	224
ALUMINUM	10×10^6	23.9×10^{-6}	239
MOLYBDENUM	50×10^6	4.9×10^{-6}	245
IRON	28.5×10^6	11.7×10^{-6}	334
COBALT	30×10^6	12.3×10^{-6}	369
NICKEL	30×10^6	13.3×10^{-6}	399
BERYLLIUM	37×10^6	12.4×10^{-6}	460

Table 2

Summary of Joining Problems

Beryllium - Prevention of cracking at welds.

Titanium - Low ductility of welds in high strength alloys.

Brazed honeycomb panels - Assembly of large structures by welding.

High strength steels - Better ductility in welds and more sensitive non-destructive inspection methods.

High temperature alloys - More data on hot cracking and strain age cracking at welds.

Refractory metals - Poor ductility of welds in both molybdenum and tungsten. More ductile welds in the high strength columbium alloys. Weldable high strength tantalum alloys.

EFFECTS of SULFUR on HOT DUCTILITY, SAE 4340 WELD METAL

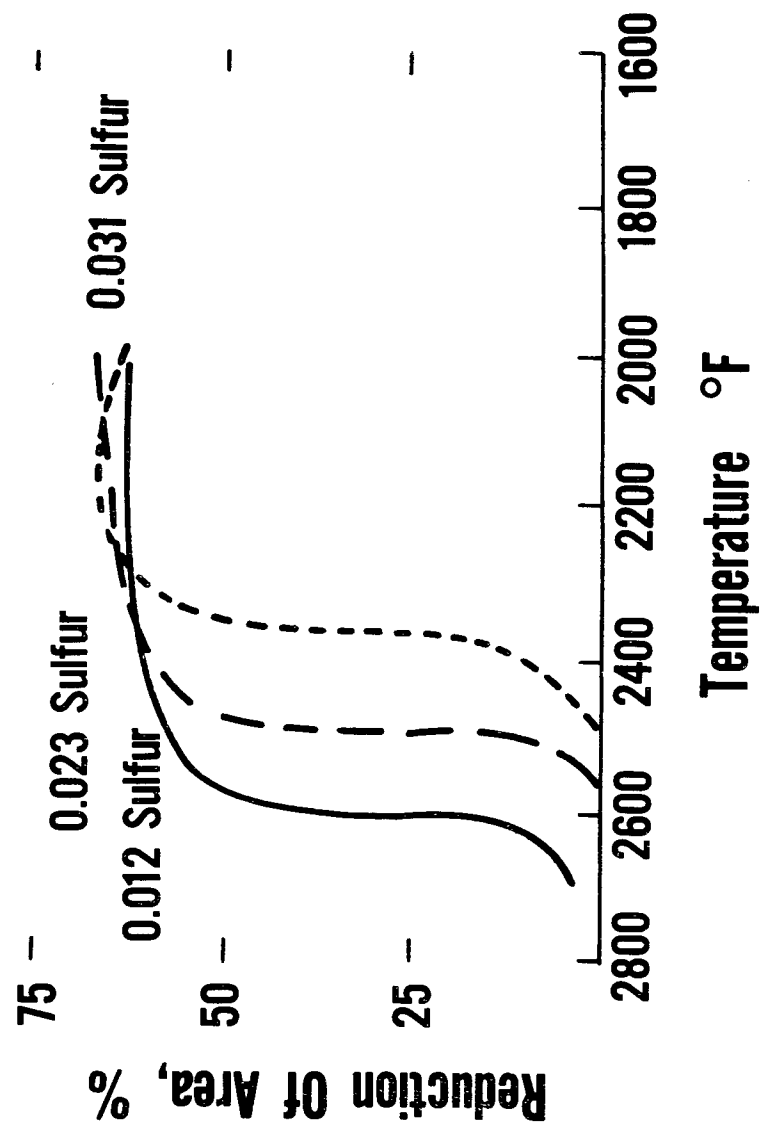


Figure 1.

TTT CURVES for 300M and 4340 STEEL

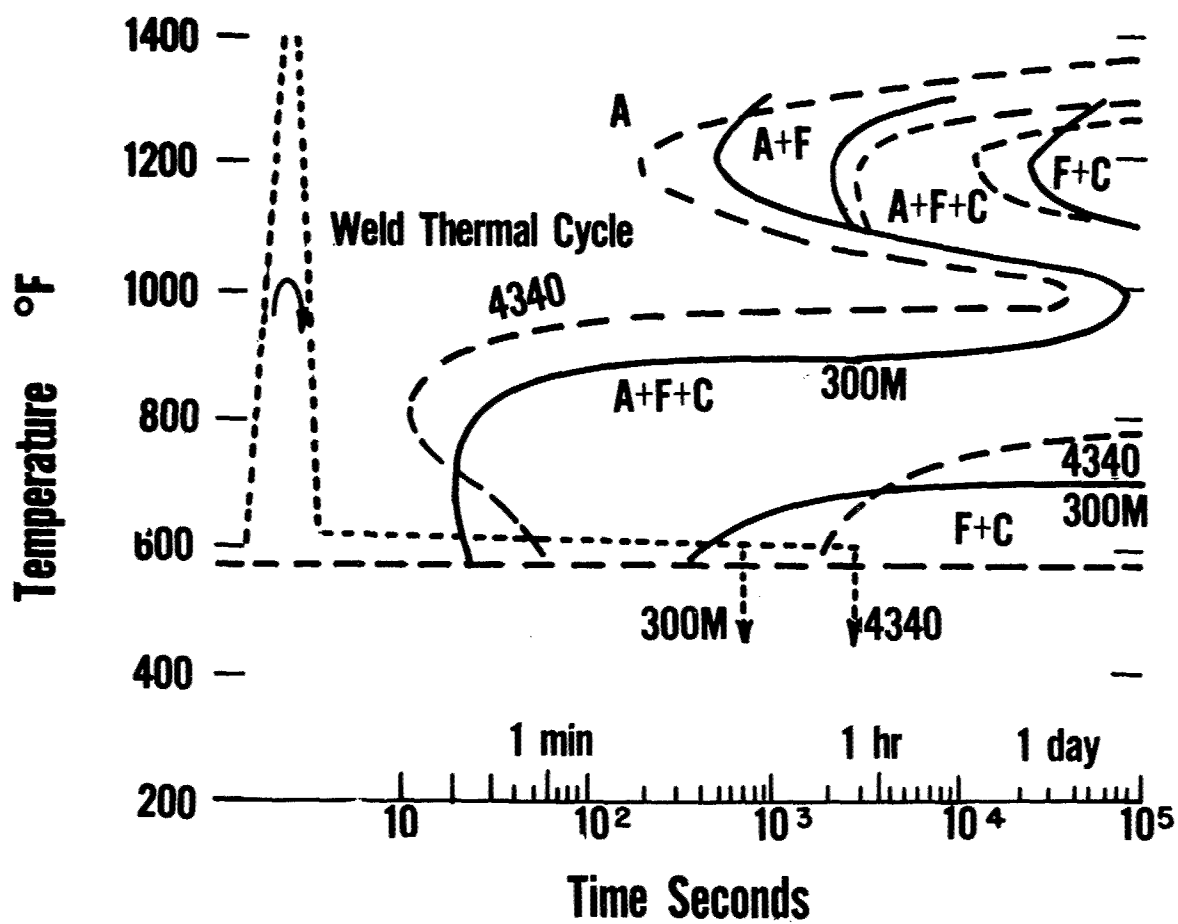
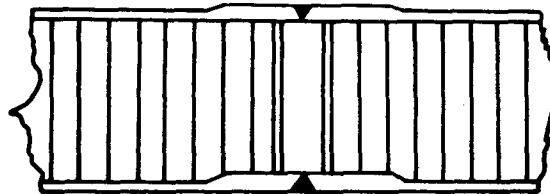


Figure 2.

ASSEMBLY of BRAZED PANELS by WELDING

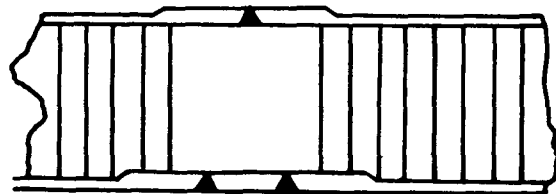
Access On Both Sides

▲ Assembly Welds



Access On One Side

▲ Assembly Welds



Cover Plate

Figure 3.

CRACKS IN ULTRASONIC WELDS



0.015 in.

Mo-0.5% Ti

0.015 in.

Mo-0.5% Ti

Figure 4.

CERAMICS AND INTERMETALLICS

Chairman	Mr. W. G. Ramke
Speaker	Mr. J. Latva
Panel Members	Mr. J. J. Krochmal Lt. C. T. Lynch

CERAMICS AND INTERMETALLICS

I. D. Latva

Directorate of Materials and Processes, ASD

Introduction

This report covers the state of the art, applications, and future requirements of the refractory ceramics and intermetallic compounds of most interest to the Air Force for structural and non-structural considerations. Materials for electronic and electrical uses are not included.

An Ad Hoc committee of the Materials Advisory Board, National Academy of Sciences, and National Research Council recently completed a thorough study of the state of the art of refractory inorganic nonmetallic structural materials on request of the Office of the Director of Defense Research and Engineering. Because of the thoroughness of the study and excellence of the report, Report MAB-169-M, permission was requested and received from the Office of the Director of Defense Research and Engineering to use selected major portions of the MAB Ad Hoc Committee report. The following sections of the MAB report were used practically intact: Borides, Beryllides (the only intermetallic compounds the Ad Hoc Committee felt were of interest as structural materials), Carbides, Nitrides, Silicides, Oxides, and Brittle Behavior (the section which treats certain problems as microstructure, fracture and flow phenomena, etc., which were common to all the material classes).

The Ad Hoc Committee was composed of the following individuals: Dr Wingate A. Lambertson - Chairman (The Carborundum Company), Dr Neil N. Ault (Norton Company), Mr John C. Bowman (National Carbon Research Laboratory), Mr Samuel W. Bradstreet (Armour Research Foundation), Mr Winston H. Duckworth (Battelle Memorial Institute), Dr Einar P. Flint (Arthur D. Little, Inc.), Dr William W. Shaver (Corning Glass Works), Dr Hans Thurnauer (Minnesota Mining and Manufacturing Co.). The consultants to the Committee were: Dr R. T. Dolloff of the National Carbon Research Laboratory (Carbides), Mr Wilfred H. Dukes of the Bell Aerosystems Company (Structures and Design). The Materials Advisory Board Staff Consultant was Mr Jerome J. Krochmal (on loan from the Air Force).

Borides

The borides are a highly refractory group of ceramic materials characterized by extreme hardness and high electrical conductivity to high temperatures. They have not been studied extensively and, as a result, data on composition and melting points are often incomplete. There appear to be more than 30 binary borides with melting points greater than 2000°C (3632°F). Those of most interest as structural materials are zirconium boride (ZrB_2), titanium boride (TiB_2), niobium boride (NbB_2), tantalum boride (TaB_2), hafnium boride (HfB_2), and thorium boride (ThB_2). Exhibiting more promise than the binaries are the mixed borides of at least ternary systems.

Titanium diboride and zirconium diboride powders and simple fabricated shapes are available in commercial quantity from several suppliers at about \$10/lb, but the other

borides are essentially experimental materials. The application of these borides has been limited since there has been no demand for these materials in commercial quantities.

The techniques ordinarily used for fabrication of parts from these borides are either molding and sintering, or hot pressing. Coatings of the borides have been prepared by flame-spraying with arc plasma equipment. High density products of these materials can now be made by hot molding which is a commercial process suitable for making simple shapes up to 1-1/2 feet in diameter and approximately the same height. Literature data on strength properties of these materials were obtained on products fabricated by hot pressing. The purity of such products is usually greater than 97 per cent, but very little work has been done with really high purity material.

Ten years ago some government-sponsored research was done on metal-bonded borides for use as turbine blades. This work showed that the metal-bonded borides did not have sufficient impact resistance for this application. The metal bond used in these studies limited their use to about the softening temperature of the alloy. Within the last two years, data generated from several sources indicates promising properties for the borides. Considerable work is being done in industry on the use of titanium or zirconium boride as cathode bars for aluminum reduction cells. These materials have also been used for aluminum vaporizing boats.

One disadvantage of the borides is that, like most inorganic nonmetallic materials, they do not have toughness at room temperature. They are probably not ductile at any useful temperature. The high strength and the hardness of the borides are desirable properties of the materials but also disadvantageous in another respect because they make them hard to fabricate. Fabricated pieces cannot be machined; finishing operations require diamond grinding.

Properties

It should be repeated that the data on borides are limited and ultimate potentials have not been fully determined.

Chemical Stability

Borides are stable compounds to very high temperatures, and are inert to the oxides. Titanium and zirconium borides are known to be stable in the presence of tungsten, molybdenum, and graphite. Thus the borides should be excellent materials to use in composite structures because they are compatible with and can be used in contact with other structural materials to extremely high temperatures.

Of the simple borides, zirconium and titanium diborides have the best oxidation resistance, being resistant to 1300°C (2372°F) and 1400°C (2552°F), respectively, for extended periods of time. Boron, which oxidizes to a glass-forming oxide, promotes oxidation resistance of the borides and there is good evidence that even better oxidation resistance can be obtained by additions to the boride compositions. It is also likely that higher temperature-stable oxide coatings can be produced on the borides more readily than on metals or carbides.

A dramatic example of an improvement in oxidation resistance is obtained from a body made of 90-percent zirconium boride and 10 percent molybdenum disilicide. The rate of oxidation of this material after one hour at 1950°C (3542°F) is 40-45 mg/cm²/hour. After one hour under these conditions an oxide layer 0.6 mm thick is formed. The oxidation rate

for a four-hour oxidation test at 1950°C (3542°F) is 16 mg/cm²/hour and the oxide layer is about 1 mm thick. At lower temperatures, the oxidation rates are considerably reduced.*

Mechanical Properties

The flexural strength of titanium diboride at 96 percent of theoretical density has been observed at 35,000 psi from 25°C (77°F) to 2000°C (3632°F). The modulus of elasticity of this product was 60×10^6 psi, and the hardness 3300 kg/mm² Vickers** (comparable to Knoop). The compressive strength of titanium diboride from another source has been measured at 97,000 psi. For zirconium boride, modulus of rupture values are reported from 8,000-29,000 psi. These are inconsistent with tensile strength values in the literature of 28,700 psi. The modulus of elasticity is reported as 50×10^6 psi.

Some data are available on the mechanical properties of the 90 percent zirconium boride, 10 percent molybdenum disilicide body discussed above. This composition has a modulus of rupture of 38,800 psi at room temperature which decreases to 13,000 psi at 1500°C (2732°F). The modulus of elasticity of this product at a density of 5.74 g/cc is 46×10^6 psi.

Thermal Properties

Thermal conductivity data near room temperature show values of 0.03 to 0.06 cal cm sec⁻¹ C⁻¹ with a positive temperature coefficient for the borides of titanium, zirconium, tantalum, and niobium.

The electrical resistivity of the borides also has a positive temperature coefficient and the borides are good electrical conductors. The resistivities of zirconium and titanium diborides are approximately 10-20 micro-ohm centimeters at room temperature.

The thermal expansion coefficient for zirconium boride is 7.3×10^{-6} /C from room temperature to 1000°C (1832°F) and for titanium boride is 8.1×10^{-6} /C to 1000°C (1832°F).*** Table 1 gives literature data on melting points.

Recently initiated efforts sponsored by the Department of Defense are expected to provide the thermochemical kinetic information which is required for theoretical evaluations on the use of the borides of hafnium and zirconium under conditions of vacuum, atmospheres of O₂, O₂ + H₂O, F₂, HF, Cl₂, N, NH₃, CO, or H₂, and temperatures to 2750°C (4982°F).

Thermal Shock

Considering the thermal and mechanical characteristics, the borides are expected to have relatively good thermal shock resistance when compared with other ceramic materials.

It is interesting that a thermal cycling test on the 90 percent ZrB₂, 10 percent MoSi₂ body showed a 50 percent increase in strength after 30 cycles from room temperature to 1350°C (2462°F) with cooling in an air blast, whereas an alumina specimen failed after two cycles.

* Unpublished Carborundum Company data.

** Unpublished National Carbon Company data.

*** Unpublished Norton Company data.

Potential Properties

The property data on the borides is very meager, and their potential is just becoming evident. On the basis of recent determinations on titanium boride, the strength-weight ratio is not exceeded by any other bulk material from 1600°C (2912°F) to above 2000°C (3632°F) and this high strength is probably maintained to at least 2200°C (3992°F). The borides are just beginning to be studied in detail, and the data to date is for borides of 98-99 percent purity.

The borides appear to be the only materials which can be used under the oxidizing conditions, supporting substantial loads for an extended period of time from 1600°C (2912°F) to 2200°C (3992°F). They will probably be used below and above these temperatures as well, but below 1600°C (2912°F), they must compete with refractory metals and intermetallics, and above 2200°C (3992°F), with graphite and the carbides.

Boride References

1. Brewer, Sawyer, et al, "A Study of Refractory Borides," J. Amer. Cer. Soc., Vol 34, No. 6, pp 173-179, (1951).
2. Campbell, I. E., "High Temperature Technology," John Wiley and Sons, Inc., New York, (1956).
3. Smiley, Sobon, et al (Standard Research Institute), "Mechanical Property Survey of Refractory Nonmetallic Crystalline Materials and Intermetallic Compounds," WADC Technical Report 59-448, January 1960.

Beryllides

The beryllides, having first been considered during the middle 1940's under the NEPA Program, constitute a fairly new addition to the many classes of refractory materials. Activities were curtailed until about 1956 when a comprehensive literature survey of approximately 800 binary systems was accomplished, resulting in the selection of about 70 compounds with melting points of higher than 1400°C (2552°F) having potential for satisfying a combination of structural and nuclear requirements. A number of these compounds which included aluminides, silicides, beryllides, zirconides, germanides, chromides, and ferrides, were screened experimentally and several silicides, aluminides, and beryllides passed initial oxidation screening tests in the temperature range of 1260°C (2300°F) to 1370°C (2498°F) by exhibiting less than 2 mils penetration after 100 hours of exposure. Continued and accelerated activity was directed toward structural as well as nuclear application potential. Minimum temperature levels prerequisites were considered also, resulting in finally limiting activity to the beryllides and silicides. Silicides, except for comparison, will not be discussed here, since they are considered as another class of materials warranting individual attention.

State of the Art

The most promising beryllides appear to be those of zirconium, hafnium, niobium, molybdenum, and tantalum. Available data indicate that the more oxidation resistant compounds are the higher beryllides such as M_2Be_{17} , MBe_{12} , and MBe_{13} . Mixtures of beryllides in a given reactive metal system will normally exhibit, in addition to excellent

oxidation resistance, considerably higher strengths than can be attained with any compound in that system (see figure 1). Excellent crystallographic work has been evidenced by the identification of these complex species.

Efforts to date have employed mainly impure starting materials, primarily Be, with major impurities being BeO (1.5%), Be₂C (.15%), and Fe (.08%). These impurities appear in the microstructure, both at the grain boundaries and as individual grains. Some attention has been given to microstructure, although most variations in grain size have been in the range of 10 to 25 microns. Recent activity has been directed toward achieving higher purities, but little or no accompanying property data is yet available. The purer beryllium powders are still rather dirty in comparison to what one thinks of in terms of high purity metal powders.

Melting point determinations have been accomplished and are generally cited as accurate to within $\pm 50^{\circ}\text{C}$ (90°F). Considering the melting point data from different facilities, there is generally agreement to within $\pm 75^{\circ}\text{C}$ (135°F), the principal difficulty is compositional changes due to the high vapor pressure of beryllium.

Continued investigations of mechanical properties (primarily modulus of rupture), oxidation resistance, and Young's Modulus, indicate that maximum utilization temperatures for the compounds of interest fall within the range of 1150°C to 1620°C (2102°F to 2948°F).

Thermal expansion coefficients, thermal conductivities, and heat capacities have been and are being determined. Oxidation studies have given primary consideration to the use of "laboratory" air but efforts are underway to elucidate the effects of wet air upon the BeO scale formed during the oxidation process. The kinetics and mechanisms of the oxidation processes are being studied or will be studied in the near future.

The process employed in the fabrication of shapes is hot-pressing with maximum pressures of approximately 2,000 psi at temperatures of 1540°C to 1650°C (2804°F to 3002°F), resulting in compacts ranging from 97 to close to 100 percent of the absolute density. Other ceramic fabrication processes, as well as mechanical working are being investigated.

Current Applications

Beryllides are currently not in use but offer excellent potential for early utilization in nuclear applications and other applications requiring high strength-to-weight ratio materials that have inherent oxidation resistance as well as thermal shock resistance to temperatures of 1620°C (2948°F). Potential applications would include leading edges, wing and body panels, nose cone skirts, bearings, supporting structures in hot areas of propulsion systems, etc. Utilization in space applications such as radiators, sinks, hot structures, etc., probably cannot be considered at temperatures in excess of 1540°C (2804°F) due to the expected deleterious effects of "hard" vacuum.

Advantages and Disadvantages

High strength, light weight, good oxidation resistance, and good thermal shock resistance, place the beryllides in a favorable position for satisfying potential requirements for materials in the temperature range to 1650°C (3002°F). Since advantages and disadvantages are meaningful in only a relative sense, a discussion must include those materials which are seemingly competitive on an "across-the-board" basis, viz, the silicides including that of carbon (SiC) and the refractory metals when suitably protected.

The beryllides have a very favorable degree of oxidation resistance when compared with the silicides, each of which (MoSi_2 , TaSi_2 , and WSi_2) exhibits the formation of a "pest." While a high temperature preoxidation treatment will preclude the formation of these "pests", such treatment is analogous to the protection afforded by a coating which is amenable to damage.

With regard to strength, it would appear that insufficient data are available to truly compare the beryllides with the silicides. Table 2, however, does indicate, even though on the basis of a very meager number of data points, that the beryllides are competitive with the silicides on a strength-density basis. Comparing the beryllides with silicon carbide, it is noted that relative strengths plus the ability of the beryllides to yield locally in regions of stress concentrations, would favor the beryllides over the most advanced form of silicon carbide available today (i.e., KT silicon carbide). The beryllides also offer, as a future possibility, some room temperature ductility which, in all probability cannot be expected from silicon carbide, a covalently-bonded material.

Competition from the refractory metals would be primarily from suitably protected molybdenum (or its alloys) which, although perhaps brittle at lower temperatures, is nevertheless quite ductile when compared with the beryllides. One hundred hour oxidation tests at temperatures from 1480°C to 1600°C (2696°F to 2912°F) are beyond the capability of even the best molybdenum coatings available to date, and years of activity devoted to this problem seemingly indicate that future progress will be meager or perhaps nil. In contrast, the beryllide picture is one of optimism, and justly so, for the elimination of a substantial percentage of impurities contained at present, and the benefits that are logically to be expected from microstructural improvements, will tend to improve low-temperature ductility.

The cost of beryllium powder is at present approximately \$79 a pound and would in all probability be substantially higher if it were obtainable in higher purity than that cited previously. If beryllium comes into widespread use as a metal, the supply factor could conceivably reach critical proportions; however, the potential beryllide utilization will probably constitute such a small fraction of industrial beryllium capacity that the supply variable is really of little significance. It is also noted that new ore deposits have been and are being discovered, and although assays are low by present standards, it is not unreasonable to expect technological improvements to permit efficient extraction.

No discussion of the pros and cons of anything containing beryllium is complete without a few words relative to the strict dust control procedures necessary to avoid toxicity hazards. It has been shown in a number of current beryllia facilities that sound industrial hygiene practices are really all that are required to cope with this problem.

Properties

Chemical Stability

The higher beryllides have varying degrees of oxidation resistance to 1600°C (2912°F) as illustrated in figure 2. Table 3 presents some short-time, high temperature, oxidation resistance data for the beryllides and silicides. The superiority of the silicides at 1650°C (3002°F) is evident. The oxidation-resistant characteristics of the beryllides are attributable to the formation of a tenacious BeO film separated from the original beryllide composition by a beryllium-depleted film. Oxidation characteristics at 1650°C (3002°F) may be described more accurately as degradation due to the high vapor-pressure of beryllium.

Physical and Mechanical Properties

Table 2 cites some typical physical and mechanical properties of both selected beryllides and silicides. Figure 1 indicates mechanical property trends and it should be noted that there is a paucity of data for temperatures below 1260°C (2300°F).

Thermal Shock

Thermal shock resistance is reported to be good when specimens are cycled between room temperature and 1260°C to 1620°C (2300°F to 2948°F). Some poor thermal shock resistance has been noted when specimens have been cycled between room temperature and 870°C (1598°F) and it is noted that this temperature coincides with the lowest exhibited modulus of rupture values.

Potential Properties

Considering the attached modulus of rupture versus temperature plots and recognizing that densities are not theoretical, grain sizes are fairly large, and in addition, that impurities are scattered throughout the structure in the form of massive agglomerates, it is reasonable to expect at least a twofold improvement in mechanical properties with some success in the correction of such deficiencies. Improvements that may be expected from ultra-high purity, which will eliminate grain-boundary impurities and the dispersed agglomerates are:

- a. Improved low-temperature strength (presently contained agglomerates constitute stress raisers)
- b. Improved high-temperature strength (creep at high temperatures may be attributed to grain boundary impurities)
- c. Improved ductility at low temperatures
- d. Improved ductility at higher temperatures

Mechanical working offers additional possibilities to improve strengths. Modulus of rupture values of 50,000 to 70,000 psi at room temperature for the lower density beryllides or from 90,000 to 125,000 psi for the heavier beryllides, will result in strength-density ratios of from 500,000 to 700,000 inches while at 1510°C (2750°F), modulus of rupture values of 40,000 and 72,000 psi for the lighter and heavier beryllides, respectively, will result in a strength-density ratio of 400,000 inches. These values are considered within reach of the better beryllides.

Oxidation resistance will be improved to a minor degree with the $\frac{1}{2}$ to $1\frac{1}{2}$ percent increase in density to the 100 percent value.

Alloy compositions are anticipated which will provide improved low-temperature ductility and the resultant compromise of high-temperature strengths, though significant from an overall standpoint, may still provide 10,000 psi modulus of rupture at 1510°C (2750°F).

The beryllides also offer promise for use both as coatings and diffusion barriers for refractory metal protection.

Beryllides References

1. Paine, Stonehouse and Beaver, "An Investigation of Intermetallic Compounds for Very High Temperature Applications," Brush Beryllium Company, WADC TR 59-29, Part I (January 1960); Part II (July 1960).
2. Booker, Paine, and Stonehouse, "Investigation of Intermetallic Compounds for Very High Temperature Applications," Progress Reports Nos. 1 (15 Aug 1959); 2 (15 Nov 1959); 3 (15 Feb 1960); 4 (15 April 1960); 5 (15 July 1960).
3. Beryllide Conference, Cleveland, Ohio; 1, 2 June 1960; Proceedings to be published.

Carbides

The highest melting temperatures known today are found among the carbides. Interest in the carbides of the transition metals, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W, and in the carbides of B, Be, Si, U and Th, stems mainly from the high melting temperatures, which indicate potentially high service temperatures, and from the high values of measured hardness, which predict very high ultimate strengths. Achieving hardware of high service temperature and high strength in these materials has not been satisfactorily met at present because of the great difficulties encountered in the chemical synthesis of characteristic, clean materials and in the reproducible fabrication of these materials into useful shapes. The magnitude of the difficulties is directly related to the high melting points — the characteristic which created the high interest.

State of the Art

Almost without exception the carbides of today are formed by powder methods. The same high melting points that predict ultimately high service temperatures make it necessary to use high temperatures in forming the basic materials and in fabricating them into useful shapes. Today's carbides are usually the result of arbitrary mixtures of particles, generally of unknown size distribution, and of a chemical nature only 98 percent defined. These are sintered or hot-pressed under a protective atmosphere which may contain an unknown amount of oxygen, nitrogen, or other active gases. The unknown 2 percent of the article may consist of any number of impurities or unidentified phases. Usually little is known about the surface layers on the particles either before, during, or after processing, because of the difficulties associated with identification. The measured properties, on the other hand, depend as much on these intergranular phases as on the basic material. The problem is thus similar to that of the ceramic oxides, but it is complicated by the fact that surface oxides in carbide bodies represent foreign, and usually detrimental, phases.

Techniques for the formation of carbide shapes have improved somewhat in the past decade to the point where reasonably high densities can be obtained in simple geometrical shapes. Such processes, however, usually require the use of high pressures at high temperatures. More complicated shapes can be obtained by precompaction, followed by sintering, but here final density is sacrificed with resultant general deterioration in mechanical strength and corrosion resistance.

Current Applications

Cobalt-bonded tungsten carbide is widely used as a cutting tool material because of its toughness at moderately high temperatures. This material is specialized, however, in that many of its useful properties stem from the binder used and, as a consequence, it is limited by the binder. Similar binders have not been found for other carbides and specific properties required for the binder phase are not recognized clearly.

The self-bonded carbides do not enjoy widespread use because they are difficult to fabricate, the cost is relatively high, and they are brittle. Many applications to date have been restricted to coatings where the abrasion resistance, hardness, and generally good chemical resistance are useful. Applications outside the coating area include crucibles for laboratory use where special chemical properties at high temperatures are required. In addition, the materials are employed where simple geometrical shapes are suitable. Examples of these include controlled resistivity SiC for heating elements, low density SiC for kiln furniture, and UC_2 rods for nuclear fuel elements. The fuel rod application usually requires a clad material for the purpose of retaining the fission products.

Advantages, Disadvantages, and Limitations

The melting temperatures of the carbides are higher than those of any other class of materials. Carbides must, therefore, be considered for use at temperatures where most materials are no longer solid and structural elements are needed.

Favorable characteristics of carbides include excellent chemical stability toward other materials, high hardness, good abrasion resistance, and reasonable strength at moderately high temperatures. A limiting characteristic is oxidation resistance. With the exception of SiC, which has a use temperature of 1600°C (2912°F) under oxidation conditions; none of the carbides can be used at temperatures exceeding 1000°C (1832°F) for long-time periods when oxygen is present.

Lack of ductility is also a limiting carbide property. While there is hope that brittleness can be reduced by close control of impurity phases and by close attention to particle shape, size, and distribution, there is no scientific evidence that this class of materials can be made nonbrittle. To date there has been no systematic approach to the problem by means of fundamental investigations of the mechanical properties of well-characterized, high purity samples. The similarity of the crystal structure of the transition metal monocarbides to that of the ductile metals, taken together with the existence of at least partial metallic bonding in these carbides, lends hope to the thesis that these materials may be inherently nonbrittle. On the other hand, the observed relations between brittle fracture and perfection of surfaces make it clear that the translation from nonbrittle laboratory specimens to full-scale, nonbrittle hardware may never be successfully accomplished.

Other difficulties with the carbides include the hardness and abrasion resistance. These properties (assets in the finished articles) act as handicaps in the fabrication processes. Shaping must be accomplished prior to final synthesis because machining is difficult. Thus, geometrical tolerances are obtained only at greatly increased expense.

Properties

The following paragraphs present a brief summary of the chemical and physical properties of the refractory carbides. Ranges of properties, rather than specific tabulations,

are given because many of the data are incomplete and because many of the reported values are strongly dependent on specific sample preparation methods.

Chemical Stability

The transition metal carbides of the fourth, fifth, and sixth columns and the carbides of B, Be, Si, Th, and U, are stable compounds having relatively large negative heats of formation. In comparison with oxides, borides, and nitrides, the carbides fall below the more stable oxides, above the nitrides, and are roughly equivalent to the borides.

The oxidation resistance of the carbides is not outstanding; the majority oxidize readily at temperatures approaching 1000°C (1832°F). Protective coatings are necessary for continued use at this temperature. SiC is an exception to this rule in that the oxidation product serves as a protective coating which permits use temperatures as high as 1600°C (2912°F) for extended time periods.

The carbides are chemically inert at ordinary temperatures. They resist reducing atmospheres and they volatilize only very slowly under vacuum conditions at temperatures approaching their melting points.

The carbides are fairly stable toward nitrogen. TiC for instance, has been reported in nitrogen at 2500°C (4532°F). One of the highest melting carbides, TaC, is unaffected by nitrogen to 3000°C (5432°F) provided there is no hydrogen present.

Strength and Modulus of Elasticity

Room temperature mechanical data on the carbides show a considerable variation from specimen-to-specimen. Reported moduli of elasticity vary between 30×10^6 psi for Mo₂C to 100×10^6 psi for WC with variations of as much as 75 percent of the mean for any particular carbide. Tensile strengths range from 5,000 to 80,000 psi; compressive strengths vary from 80,000 to 600,000 psi and flexural strengths cover the interval from 10,000 to 120,000 psi with variations as high as 85 percent of the mean for given carbides.

Strength measurements at temperatures above 1500°C (2732°F) have been made for only a limited number of carbides. SiC flexural strength is practically unaffected up to temperatures of 1500°C (2732°F) with values as high as 70,000 psi reported. Cr₃C₂ shows an increase in flexural strengths, with increasing temperature, from about 43,000 to 80,000 psi at 1100°C (2012°F), followed by a sharp decrease at higher temperatures. B₄C, ZrC, and TiC all exhibit decreased flexural strength with temperature increase to 1200°C (2192°F) or higher. In only a few cases have measurements been carried out at temperatures up to 2000°C (3632°F) with strength values reported in the range of 20,000 psi in flexure for mixed carbides.

High-temperature moduli of elasticity have been reported for SiC and Be₂C. For Be₂C the modulus drops from 26 to 12×10^6 psi as the temperature is increased to 1100°C (2012°F). For SiC the modulus decreases slightly or increases, depending on the sample, to a 1550°C (2822°F) value of about 40×10^6 psi. No high-temperature modulus of elasticity data have been reported for the other carbides.

It is apparent that data on high-temperature strengths and moduli of elasticity are scarce in the range up to 1500°C (2732°F) and practically nonexistent at higher temperatures. More of this data is needed for a valid evaluation of carbide potentials. The influ-

ence of grain size, growth and orientation, as well as density and type of porosity, must also be evaluated further.

Thermal Properties

The highest reported melting point, 3940°C (7124°F), is for the complex carbide, 4TaC:HfC. Six of the simple carbides, TiC, ZrC, HfC, NbC, Ta₂C, and TaC melt at temperatures in excess of 3000°C (5432°F) and most of the others under discussion melt above 2000°C (3632°F).

Coefficients of thermal expansion range from a low of $4.5 \times 10^{-6}/\text{C}$ for B₄C and SiC to a high of $12.5 \times 10^{-6}/\text{C}$ for UC₂; thermal conductivities are as low as 0.034 cal/cm sec C for CbC and as high as 0.1 cal/cm sec C for SiC; specific heats have a low of 0.04 cal/g C for WC and a high of 0.16 cal/g C for SiC; thermal emissivities, for which data is very incomplete, range from 0.2 to 0.4.

The majority of this thermal data is subject to the same criticisms as the mechanical data. They depend strongly on the nature of the sample, its chemical composition, purity, grain size and distribution, density, and porosity. With the exception of the very high melting points, and the somewhat unique characteristics of SiC, the thermal properties of carbides are not extraordinary.

Thermal Shock

With the exception of SiC, whose service range has an upper limit of about 1600°C (2912°F), none of the carbides can be classified as having good thermal shock resistance. To date, very little work has been done to determine how the factors — such as grain size and orientation, porosity type and distribution, additives phases — can be varied to improve strength and thus thermal shock properties. The first significant program to determine factors of this type in a typical carbide such as ZrC has only recently begun. The results to date are encouraging. It is not apparent, however, that orders-of-magnitude improvement will be achieved in the thermal shock parameter by manipulation of the parameters involved without possible adverse effects on other important properties such as high-temperature strength.

Potential Properties

It is difficult to predict the ultimate properties attainable in the carbides because pertinent information is not available. While many properties have been measured and reported, in almost no case has relevant data been reported on sample purity, stoichiometry, grain size, distribution and orientation, porosity or particle surface chemistry. Since the observed properties are strongly dependent on these factors and since these data are usually not known, extrapolation of the observed properties in terms of future potential cannot be accomplished with a high degree of certainty.

Temperature data in the range from 1000°C (1832°F) to 2500°C (4532°F) is particularly conspicuous by its almost complete absence. Data is needed on strengths, elastic moduli, thermal conductivities, and coefficients of expansion — all determined as functions of temperature and correlated with the sample purity, grain size, porosity, and other controlling microproperties to determine the potential usefulness of the carbides.

A single series of experiments indicates that useful high-temperature strengths can be obtained in the carbides. This observation is based on evidence that the addition of a low

elastic modulus material, such as graphite, to a carbide, such as ZrC, may improve the thermal shock parameter of the body while improving the high-temperature strength. In the cited instances, the addition of 20 percent resulted in a modulus of rupture of 9,000 psi at 1750°C (3182°F), a value twice that of the ZrC alone. The strength of the composite exceeded that of the base material throughout the entire range above room temperature.

Experiments of this nature indicate that significant progress may be expected through specific research applied to the problem of optimizing high-temperature properties in carbides. There is little doubt that careful and imaginative studies in this and related areas, on well-characterized carbide materials, will lead to structural materials with useful strengths at temperatures approaching 2500°C (4532°F).

Carbide References

1. Schwarzkopf and Kieffer, "Refractory Hard Metals," The MacMillan Co., (1953).
2. Campbell, I. E., "High Temperature Technology," John Wiley and Sons, (1956).
3. NAVORD Report 6056, "Polaris Materials Program," February, 1958.
4. Lockheed Missiles System Division Report, IMSD-2466, "Properties of Refractory Materials: Collected Data and References," January 1959.
5. WADC Technical Report 59-448, "Mechanical Property Survey of Refractory Non-metallic Crystalline Materials and Intermetallic Compounds," January 1960.
6. "Proceedings of an International Symposium on High Temperature Technology," McGraw-Hill Book Company, 1960.
7. "Study of Combinations of High and Low Elastic Modulus Ceramic Materials," Quarterly Reports 1, 2, 3, The Carborundum Company, WADD Contract No. AF 33 (616)-6806.

Nitrides

There are several nitrides known to have interestingly high melting points. Of these, the interstitial nitrides of Sc, Ti, Zr, Hf, V, Nb, Ta, Th, and U appear to be sufficiently resistant to dissociation, to consider them as refractory. Dissociation pressures of the interstitial nitrides, of Cr, Mo, and W are considered to be too high for them to be interesting. Of the covalent nitrides, Be, B, Al, and Si are refractory. Several other nitrides, particularly the interstitial nitrides of La, Ce, Pr, and Nd, are suspected of being refractory enough to consider here, but data on their melting and dissociation temperatures is lacking.

State of the Art

Of the refractory nitrides, commercial products are made only of BN, AlN, and Si₃N₄, and the production of these is limited. Probably the commercial status can be summed up, more or less, for each as "potential applications are being explored"

There has been little Government research on refractory-nitride ceramics. TiN and ZrN were investigated as crucible materials and, cursorily, for rocket nozzles several years ago, and the AEC has looked at UN ceramic for use as nuclear fuels.

Advantages and Limitations

The nitrides are not notably oxidation resistant. This deficiency and, except for the case of BN, no clearly unique qualities account for the inactivity on nitride ceramics. With the exception of Si_3N_4 , none could be recommended unequivocally for use in air above 1100°C (2012°F). The nitrides of Be, Al, Sc, La, Ce, Pr, Nd, Th, and U also are reported to react with water vapor.

Because it has crystal structures similar to graphite and diamond, with slightly better oxidation resistance than the other nitrides, BN is probably the most interesting for structural use. Efforts to self-sinter hexagonal BN powder have been unsuccessful, and like graphite, bodies made from it to date contain a binder. Data are available on a body* containing 2.4 percent B_2O_3 made by hot pressing. It has several similarities to graphite:

1. Directionality in properties.
2. Easily machineable, but not quite so soft as graphite.
3. High thermal conductivity (100-200 Btu/ft²/in/hr/ $^\circ\text{F}$).
4. Excellent resistance to thermal shock.
5. Slight resiliency.
6. Low density (body density - 2.1 g/cm³; crystal density - 2.25 g/cm³).

Its room-temperature strength (15,900 and 7,300 psi modulus of rupture, depending on direction) is somewhat higher than that of graphite. But, in the range from about 982°C (1800°F) to 1482°C (2700°F), the strength drops to 1000 - 2000 psi. At higher temperatures the strength increases, approaching the room temperature value at 2400°C (4352°F). This rather odd strength-temperature behavior, characteristic of oxide-bonded BN, is closely associated with the binder.

Unlike graphite BN is an electrical insulator which, depending on the application, could be advantageous. The resistivity of the above body is reported to be:

TEMPERATURE, C	RESISTIVITY, ohm - cm
25 (77°F)	10^{13}
500 (932°F)	10^{10}
1000 (1832°F)	10^5

In another experiment a resistivity of 10^{14} ohm-cm at 500°C has been reported.

BN is reported to have excellent oxidation resistance to 700°C (1292°F), and not to be wetted by many molten metals and salts. A disadvantage is its tendency to hydrolyze; its performance as a rocket nozzle, for example, is improved by thorough drying before testing.

* Carborundum Company

Cubic BN has been made by methods used to produce synthetic diamond, and has a hardness in the range of diamond.

Concerning the other refractory nitrides, moduli of rupture of 11,500 and 20,000 psi were reported for ceramics of AlN and Si_3N_4 , respectively, at room temperature. Another AlN ceramic prepared by hot pressing was reported to have a modulus of rupture of 38,500 psi at room temperature and 18,000 psi at 1400°C (2552°F); its modulus of elasticity at room temperature was 50×10^6 psi. A ceramic of Si_3N_4 was reported to lose "little" strength with temperature increases to 1100°C (2012°F). Thermal shock resistance of AlN or Si_3N_4 is reported to be "good".

Silicides

State of the Art

Methods that have been or can be used in preparing the silicides in powder form are the following: (1) synthesis by fusion or sintering (2) reduction of metal oxides with silicon (3) reaction of metal oxides with SiO_2 and C (4) reduction of mixtures of silica and metal oxides by means of a thermite reaction (5) reaction in a molten alloy (6) reaction of metal with silicon halide or metal halide with silicon, or simultaneous decomposition of metal and silicon halides, and (7) fused salt electrolysis.

Pure silicides can be formed by sintering together a finely-divided mixture of silicon and the appropriate metal, if sintering is sufficiently prolonged and if there is intermediate grinding and remixing between several sintering steps to assure homogeneity. The simultaneous thermal decomposition of a mixture of a volatile metal chloride with one or more of the silanes should be capable of producing pure metal silicides.

Once the silicides have been prepared in pure form, it is necessary to exercise care in subsequent processing. With molybdenum disilicide, for example, it is necessary to crush and grind the material in a neutral atmosphere or under an unreactive liquid. Otherwise, even with the moderate amount of heat developed during these operations, oxidation of the surface of the disilicide particles will occur.

Current Applications

Only a narrow range of applications has been found for any of the silicides. Molybdenum disilicide has received much study as a coating for molybdenum and other materials that are susceptible to oxidation at moderate to high temperatures, but this application is not considered here since it falls within the category of composite materials.

The most notable use for molybdenum disilicide as a bulk material has been as a major constituent of resistance heating elements that can be brought to temperatures of 1650°C (3002°F) in an oxidizing environment. Other uses suggested for molybdenum disilicide shapes are in thermocouple protection tubes (for measurement of hot exhaust gases and molten bath temperatures), crucibles, and other refractory shapes (for molten materials such as glass).

Test specimens of molybdenum disilicide have been fabricated for a study of heat-resistant materials in leading edge applications. These specimens were prepared from

impure commercial molybdenum disilicide powder and were formed by slip casting and sintering.

The major obstacles to the use of molybdenum disilicide in this application were found to be the development of considerable plasticity in the specimens at 1370°C (2498°F) and above, as well as the high creep rate of the material.

Advantages and Disadvantages

As mentioned previously, the outstanding advantages of the disilicides are their oxidation resistance at high temperatures and their maintenance of high tensile strength and modulus of rupture at temperatures where most oxides and metals have low values for these properties.

The primary disadvantages of some members of this class of materials are as follows:

1. Room-temperature brittleness
2. Excessive creep at high temperatures, at least in the case of molybdenum disilicide
3. Poor oxidation resistance at low temperatures, e.g., in the 500°C (932°F) to 900°C (1652°F) range for molybdenum disilicide.

It is not known whether all of the above are intrinsic limitations of the disilicides or whether they are brought about, to some degree, by the presence of impurities in the raw materials, by lack of the desired stoichiometric ratio, or by poor fabrication methods.

Properties

Chemical Stability

There is little doubt as to the excellent high-temperature oxidation resistance of molybdenum disilicide, tungsten disilicide, and such other disilicides as have been studied. For example, slip cast and sintered molybdenum disilicide test pieces have been subjected to air flows corresponding to mass velocities of 1500 lb/ft² hr at temperatures up to 1480°C (2696°C). Very small weight changes were noted.

Studies of the mechanism of the reaction of molybdenum and tungsten disilicides in an oxidizing environment at temperatures up to 1700°C (3092°F) or higher show that the oxidation resistance of these materials results from the formation of a glassy coating of silica over the disilicide shape. These silica coatings are firmly anchored to the disilicide base and they are self-healing so that, when a break results from impact or other stress application, the coating will renew itself during continued exposure to an oxidizing atmosphere at high temperatures.

The poor oxidation resistance shown by at least some disilicides at low temperatures can be alleviated first by oxidizing the test specimen at a high temperature to insure formation of a protective silica coating which will prevent the entry of oxygen into the interior of the specimen.

Strength

Work at Brush Beryllium Company (1) on tantalum and tungsten disilicides has indicated that these materials retain high modulus of rupture values at temperatures up to

1510°C (2750°F) as shown in figure 3. Values for molybdenum disilicide reported by Bell Aircraft Corporation (2) are also given in this figure. Tungsten disilicide is particularly noteworthy as the best specimens made from it had modulus of rupture values of close to 70,000 psi at 1370°C (2498°F) and 1510°C (2750°F), a value roughly comparable on a strength-to-weight basis to values obtained on beryllides.

Thermal Properties

Various silicides have the following melting points:

<u>COMPOUND</u>	<u>MELTING POINT</u>	
TiSi ₂	1540°C	2804°F
ZrSi ₂	1520*	2768*
VSi ₂	1750	3182
NbSi ₂	1950	3542
TaSi ₂	2400	4352
CrSi ₂	1570	2858
MoSi ₂	1870	3398
WSi ₂	2150	3902

(* MELTS INCONGRUENTLY)

Recent determinations of the mean coefficients of thermal expansion of tungsten and tantalum disilicides give a value of about 4.7×10^{-6} in/in/°F between 27°C (80°F) and 2037°C (3700°F) for both compounds.

The thermal conductivities of samples of molybdenum disilicide of 95 percent theoretical density are reported as follows:

<u>TEMPERATURE</u>	<u>K</u>
° F	BTU / hr / ft ² / F / in.
70	218
390	290
1470	145

It is to be expected that other disilicides would have high thermal conductivities.

Potential Properties

One of the more serious defects of molybdenum disilicide is its high creep rate at elevated temperatures. Although creep measurements have not been made on materials of controlled purity, it seems probable that high creep is an intrinsic property of molybdenum disilicide.

In metal alloy systems it has been found that solid solutions possess more resistance to plastic deformation than does a pure metal. Increase of the concentration of the solute

decreases the rate of creep. After the limit of solid solubility of the solute has been reached, and the excess then appears as a dispersed phase, creep is further retarded because the stress required to move dislocations is increased by the presence of the dispersed phase.

To insure persistence of the dispersed phase at elevated use temperatures, it will be necessary to have that phase present in a concentration which will exceed its solid solubility at the use temperature. Therefore, it would seem advisable to concentrate efforts on a relatively few pseudo binary systems of the silicides. One that appears promising is the WSi_2 - TaSi_2 system, both from the standpoint of the refractory nature of the end members (m.p. WSi_2 , 2150°C (3902°F); m.p. TaSi_2 , 2400°C (4352°F)) and the incomplete solid miscibility between them. It has been shown by previous investigators (3) that at 1300°C (2372°F) tantalum disilicide will take up 25 mole percent of tungsten disilicide in solid solution and that tungsten disilicide will take up about the same proportion of tantalum disilicide in solid solution. Inasmuch as the disilicides are compounds of high metallicity, it may be that the resistance to creep would be increased in these combinations as is the case in metals.

The effect of the presence of small amounts of other metalloid elements on the formation or stabilization of various crystal types and possible influence on creep and other properties deserves further investigation. Thus it is known that low concentrations of carbon, nitrogen, and oxygen can result in the persistence of certain structural types in pseudo binary or ternary systems of the silicides, over concentration and temperature ranges where such structures would otherwise be metastable.

Combinations of disilicides and diborides merit further development. The Carborundum Company has found that a combination of 90 percent zirconium diboride and 10 percent molybdenum disilicide has excellent resistance to oxidation at temperatures up to 1950°C (3542°F). Further study is needed on the silicon-boron system, as the compound SiB_6 is surprisingly refractory (m.p. 1950°C (3542°F)).

Silicides References

1. Booker, Pain, and Stonehouse, "Investigation of Intermetallic Compounds for Very High Temperature Applications," Progress Reports Nos. 2, November 15, 1959; 3, February 15, 1960; 4, April 15, 1960; 5, July 15, 1960, Brush Beryllium.
2. Dukes, Anthony, and Pearl, "Investigation of Feasibility of Utilizing Available Heat Resistance Materials for Hypersonic Leading Edge Applications," April 15, 1959, Bell Aircraft Corporation.
3. Nowotny, Kudielka, and Parthe, "The Structure of Silicides," Plansee Proceedings 1955, The Pergamon Press, London, 1956.

Oxides

Refractory oxide ceramics comprise an important class among nonmetallic refractory materials, although they are by no means among the highest melting compounds. Thorium oxide, which is on top of the list, has a melting temperature of 3200°C (5792°F), and aluminum oxide, the oxide which so far has found the widest application, melts at 2050°C

(3722°F). Melting temperature is rarely a limitation of high-temperature structural materials. Before melting occurs some other property usually becomes a limiting factor.

Refractory oxides are outstanding for their chemical stability over a wide range, especially under oxidizing conditions. They show up well in comparison with other classes of refractory materials; nevertheless, it should not be overlooked that their stability at high temperatures is also affected by conditions of atmosphere, pressure, and contact with other materials. Uranium dioxide, for instance, oxidizes to U_3O_8 at relatively low temperature in air, but it has good stability up to its melting point if heated under reducing conditions. Al_2O_3 may be mentioned as another example. It is stable in air up to 1950°C (3542°F) but dissociates slowly in vacuum above 1800°C (3272°F) to gaseous Al_2O and O_2 .

The military opportunities of oxides as structural parts arise from those properties which point toward applications beyond the usefulness of metals and for those applications where structural use is combined with thermal and electrical insulation requirements. For structural parts, deformation characteristics and stability under intermittent and continuous load and temperature are of special significance; for thermal insulation, thermal conductivity, and heat capacity, and for electrical insulation, changes of dielectric properties with temperature must be considered.

Properties of oxide ceramics depend not only on chemical composition, but also on micro- and macro-structure of the finished article. A wide variation of mechanical characteristics is obtained from single crystals and dense, single-phase polycrystalline solids. In the case of thermal insulation, structures of well-defined porosity are of advantage.

Properties

Investigators have confined their attention almost exclusively to determining the properties of the single oxides, Al_2O_3 , BeO , MgO , ZrO_2 and ThO_2 ; Al_2O_3 receiving the most attention. Among the mixed oxides, refractory silicates, aluminates, titanates, niobates, zirconates, and phosphates have been investigated. A wealth of up to date information on properties of refractory single and mixed oxides is available in WADC Technical Report 59-448 (January 1960); however, test results obtained from various sources are difficult to compare, as microstructure, porosity, chemical composition; and test conditions are not known. Only in rare cases is such complete information available. Nevertheless, a fairly good picture of properties of oxide ceramics emerges, as test refinements continue and as improvements in preparation of test specimens of higher density are made. A brief discussion of those properties which are most pertinent for structural applications is in order.

Fracture Strength

The fracture strength of refractory oxide ceramics compares favorably with that of refractory metals, especially if one considers strength-to-weight ratio. The effect of temperature on the strength of oxide bodies has not been studied intensively. The best data is available for sintered aluminum oxide which at the present state of the art, exhibits the highest fracture strengths among the refractory oxides. For instance, a tensile strength of 35,000 psi at room temperature has been reported. Eighty percent of the strength is retained up to 1100°C (2012°F). Around 1200°C (2192°F) a considerable drop in strength occurs and at 1370°C (2498°F), minimum limit of high temperature as defined for this report, only about 10 percent of the room temperature strength remains.

Other refractory oxides such as BeO , ThO_2 , MgO , and ZrO_2 follow a similar pattern; if their room temperature strengths can be brought up to that of Al_2O_3 , it may be expected that they will retain 10 percent of their strength at higher temperatures than Al_2O_3 .

In general, strength values have improved steadily during recent years, due to improvements in processing methods which have led to higher density, lower pore content, and better control of microstructure.

Impact resistance has also gone up, but not to the same extent that flexural strength and density have been improved. Major significant improvements in impact strength can only be expected as a result of solving the problem of brittle fracture of oxide ceramics. It is well-known that ductility at room temperature has been observed on certain oxide single crystals; there are no signs at present that room-temperature ductile polycrystalline oxide ceramics can be produced. It has been found that the impact strength of Al_2O_3 and MgO actually decreases between room temperature and up to 1600°C (2912°F), although plastic deformation is known to occur within this temperature range under slowly applied load.

Thermal Shock Resistance

Refractory oxide ceramics are known for their low thermal shock resistance in comparison with other materials. Improvements may be expected, but they will be only marginal unless an order of magnitude increase in strength is achieved. More important than improving physical properties, seems to be an improvement of the shape factor which also enters into the thermal shock equation. It points toward the usefulness of shapes of small cross-sectional area, such as fibers, platelets, etc., to reduce the thermal gradient.

Stability and Oxidation Resistance

The relatively high chemical and thermal stability and oxidation resistance of oxide ceramics make them attractive as materials of construction for high-temperature applications. Thorium oxide is the outstanding material which is stable in air up to 3200°C (5792°F). To make full use of the favorable high-temperature properties of oxides, it is important to use high purity materials. Small amounts of oxide impurities lower melting temperatures appreciably, as can be seen from phase diagram studies.

Vapor pressure data of oxides are fairly well established; work on the chemical interaction of oxides with varying types of gases at high temperature is in progress.

The interaction of oxides in contact with metals has been studied, but more information will be necessary. Little is known about diffusion mechanisms and rates of gas flow through oxide layers at high temperatures and under varying service conditions.

Dielectric Properties

These properties, not relevant for structural uses, but important as secondary considerations, should be mentioned, especially in the case of refractory oxides. BeO , MgO , and Al_2O_3 remain electrical insulators to higher temperatures more than any other dielectric with the possible exception of boron nitride.

Potential

A steady improvement of the physical properties of refractory oxides can be foreseen. As in former years, these improvements will come about by better processing methods, rather than by compositional changes. A recent significant achievement in this direction has been the production of pore-free, transparent aluminum-oxide ceramics by the General Electric Company. If oxide ceramics are to be used, then shape and design factors will take on considerably more importance. Ways must be found to use oxide ceramics in the form of small units of high strength, such as thin sheets, platelets, or fibers, either as built up units or in composites for reinforcements. Thin oxide sheets may be laminated between metallic sheets; platelets may be used in protective coatings for metallic or other substrates, and continuous fibers may be woven into textiles or ropes.

It seems doubtful that ceramic oxides, per se, in solid sections will find uses as structural materials, but they will be used for protection of other materials, as coatings, and for low stress applications where thermal or electrical properties are the prime consideration.

Oxide References

1. WADC Technical Report 59-448, January 1960. "Mechanical Property Survey of Refractory Nonmetallic Crystalline Materials and Intermetallic Compounds," by Stanford Research Institute.
2. Proceedings of an International Symposium on High Temperature Technology, October 1959. McGraw-Hill Book Company. Chapters on "Oxides for High Temperature Applications," by W. D. Kingery, pp. 76-89.
3. OTS PB 161194 - February 26, 1960 - DMIC, Memo 44, Refractory Materials. Defense Metals Information Center, Battelle Memorial Institute, Columbus 1, Ohio.
4. Lockheed Aircraft Corporation - LMSD-2466 - January 15, 1959. "Properties of Refractory Materials," Collected data and references.

Brittle Behavior

Design Technology

Design technology for brittle materials has not been established. This puts a major limitation on the use of brittle materials in load-bearing components. Particularly in air vehicles where weight and size are critical, one does not want to use a component that can withstand safely, for example, a 1000-pound load when the maximum load is only 100 pounds. Conversely, the component must be safe.

Present knowledge of how to design structural members with brittle materials is inadequate for their use in reasonably efficient and safe designs. An allowable stress cannot be assigned logically. It follows that knowledge of how to evaluate resistance to load (strength) of brittle materials probably is inadequate.

It is known that the stress at which a given brittle material will fracture depends on size and stress-state as well as time, temperature, and atmosphere. It is known that the

reproducibility of brittle failure stress as measured in a controlled test is poor compared with the reproducibility of yield stress in ductile failures. Although progress has been made, knowledge of these effects is inadequate for the quantitative treatment needed to design safe structures. Thus, one problem area is that of establishing relationships that adequately describe the conditions under which a load will cause a brittle material to break.

The strength behavior of brittle materials is altogether different from that of ductile materials, and failure criteria developed for ductile materials cannot be used to design with brittle materials. Unlike ductile materials, where a shear component of the applied stress causes deformation failure, a tensile component of the applied stress is critical in fracturing brittle materials. Also, once started, a fracture crack can propagate rapidly without additional load applications, whereas additional stress is required to extend a plastic deformation. In this connection, relief of a stress concentration in a brittle material by fracture permanently damages the structure, while little or no damage is caused when plastic flow in a ductile material removes a concentrated stress. As another major difference, size effects need not be considered in the failure of ductile materials.

It is widely accepted that a "flaw"* initiates fracture by concentrating stress in a localized volume. The fracture propagates when the stored elastic energy exceeds the energy required to form a new surface.

As a consequence of fracture being initiated by a flaw, unlike the case of ductile materials, strength must be treated by considering brittle materials as inhomogeneous. This is done best apparently by the so-called "statistical theories" of failure. In the statistical concept, the scatter in fracture stress from nominally identical specimens tested under the same conditions becomes an intrinsic property of each material, and strength is not defined in terms simply of stress and/or strain. Further, in this concept, one can separate into two types the external factors that affect strength:

1. The "statistical" ones (i.e., those that determine the number of flaws acted on in given material) such as size, shape, stress distribution and, perhaps, stress type (combined stress).**
2. The "material" ones such as temperature and time (strain rate, creep, fatigue).

To develop a design technology, it is necessary that we learn to handle confidently the statistical effects. Several methods have been proposed to do this. The most widely known method is the one Weibull originated. More general methods have been proposed; Weibull's and other solutions based on a failure behavior analogous to that of a chain breaking at the weakest link are special cases. These may not be statistical methods most generally useful, or most applicable to the ceramics of present interest.

Adequate experimental control is extremely difficult to achieve in investigating the "statistical" effects. This probably is the major reason that a general design technology

* In addition to the normally considered types, the flaws might be crystal-lattice imperfections, frozen-in local stresses in grains, a grain boundary, etc.

** In some recent British work, these factors have been treated from the view that a brittle material is composite, consisting of a skin and core, each with its own mechanical properties. This view is felt to warrant consideration as well as the statistical approach.

for brittle materials is not at hand. Without extreme care, uncontrolled variables in specimen preparation or in strength testing are likely to influence data and, if unrecognized, to cause erroneous conclusions. Also, peculiarities of a specific experimental material can confuse interpretation of data. For example, the marked effect of moisture on the strength of glass and periclase crystals causes doubt as to their suitability as experimental materials for developing a general design technology.

Probably the greatest need in establishing a design technology is for a body of fracture-stress data obtained under conditions of extreme control, i.e., where unknown extraneous stresses in testing or uncontrolled variables in specimen preparation have not had an influence. Controlled variables in this data should include such factors as type of ceramic, size, stress state, and perhaps strain rate.

Once the design relations have been developed, the problem of developing or selecting test methods and procedures for furnishing the data necessary to use these relations requires attention. Hence, in addition to research on determining an applicable criteria for failure, research probably will be needed on testing techniques to obtain the strength data that will allow full and proper consideration of ceramics in mechanical-design work.

Effects of Microstructure

The strength of a ceramic is known to be a function of microstructural* features, and they in turn, depend on the processing methods and conditions used to prepare the ceramic. Knowledge is incomplete concerning the microstructure that would give best strength properties, and on the effects of processing variables which determine microstructure or strength properties of a ceramic. Such knowledge could lead to ceramics with improved strength properties, and lead to their greater utilization in load-bearing applications.

Any change in processing a ceramic can be expected to affect its strength properties, and the potentialities for improving ceramics through research in this area appear to be great. Theory suggests that a flaw-free ceramic should withstand stresses in the million-psi range, whereas present ceramics fail in the thousand-psi range.

Data have been obtained showing that, in general, fracture strength increases with decreasing porosity (at least so long as pores are located near grain boundaries) and is related to grain size in a ceramic body. In some brittle materials, strength is affected greatly by surface character. There are undoubtedly other features of a brittle material that can affect strength but that are not yet recognized, such as crystal structure, grain boundary conditions, trace impurities, etc.

Present knowledge of ceramic processing is inadequate to provide ceramics in which pore removal and grain growth can be extensively controlled. Ceramics are made by compacting powders and heat treating the compacts. During the heat treating, in the refractory materials of interest, the compacted powder undergoes sintering reactions. These reactions are manifested by bonding together the powder particles, a material transport that fills pores between mismatched neighboring pores and causes certain particles to grow at the expense of others. The driving force for these reactions is the free surface energy of the particles, and the most widely held theory is that densification occurs by a vacancy-diffusion mechanism in solid-state free sintering and by viscous flow in hot pressing, or if a liquid phase develops.

* Including pore structure and, perhaps, crystal structure.

To attain ultimate strength in a ceramic it becomes quite important that we understand these sintering reactions better. By this means, sound guidance can be given to the selection of processing conditions that will yield the strongest body structure. Variables in the processing that are known to influence sintering, and whose effects require further elucidation through research, include:

1. Physical form of the starting powder
2. Contaminants
3. Compacting conditions
4. Sintering atmosphere, pressure, and temperature schedule.

Other Studies

In addition to the problems of a fracture criterion for brittle materials and of improving the strength properties of ceramics, there are other problems that require research before maximum utilization can be made of ceramics in load-bearing applications.

When the temperature is raised, a point is reached with most stressed brittle materials where plastic flow occurs, and information on this transition area is important. However, it has been studied very little. A first question demanding an answer is whether a material can sustain useful loads once the transition is reached and, if so, what strength criterion can be used in mechanical design. Another area for inquiry concerns ceramic factors, i.e., study of the effects of variables in composition and body structure of the ceramic on the conditions for, and the nature of, this pyroplastic flow.

Under special conditions, plastic flow rather than fracture is observed at room temperature in certain inorganic nonmetallics, indicating that brittleness is not an inherent quality of ceramics. Therefore, research on improving the strength properties should treat not only the problem of increasing the fracture stress, but also that of lowering the yield stress. If, for example, a change in body structure decreases the brittle strength of a ceramic but increases its tendency to yield, sufficient change in this direction might provide a ductile ceramic. Experiments in this area are hampered because there is no method for measuring the tendency to yield nominally brittle materials. However, indenter- and hydrostatic-loading techniques appear to warrant investigation. Indenter methods are additionally attractive as tools for studying brittle-strength behavior, since they offer the possibility of measuring the energy required to propagate a crack and of stressing only the interior of a ceramic body in tension, as opposed to usual methods, which apply tensile stress to the surface or to both the surface and the interior.

Applications and Requirements for Ceramics and Intermetallics

The previous sections for the most part taken from Report MAB-169-M were primarily concerned with describing the present state of the art of those refractory inorganic non-metallics that have or promise a potential as high temperature structural materials. The applications where the refractory inorganic nonmetallics have potential include such items as: wing and body panels for thermal protection, leading edges of glide re-entry vehicles, re-entry nose cones, rods for nuclear fuel elements, high temperature seals and bearing, insulative structures for hot areas of propulsion systems (ramjets and solid propellant rockets), coatings and diffusion barriers for refractory metal protection, and

electrical insulation for communication and navigation equipment. Although these items are representative, they are, however, only a fraction of the many possible applications for these materials.

It must be realized that the step from potential to actual use is a great one, one that will only come about through intensive well-planned research efforts directed to the anticipated problems associated with the advanced and future aerospace systems. What then are a few of these anticipated problems and what will be required of the structural materials in the near future?

The environmental conditions of advanced propulsion and atmospheric re-entry aerospace systems will provide an indication of the enormous magnitude of these problems and future material requirements. Of greatest concern are the induced environments, those which will be generated by the advanced systems during their flight path or operational period. The environments chosen for consideration include those of the glide re-entry vehicle, ballistic re-entry body, and solid propellant rocket motor.

Glide Re-entry Vehicle

The induced environment imposed by the specific configurations or design parameters of a glide re-entry vehicle varies in accordance with the position of the vehicle along its three phase flight trajectory, i.e., boost, orbit, and re-entry. The environment consists of various factors such as: accelerations and decelerations, noise, wind loads, shock, vibration, moderate to large dynamic pressures, large total integrated heat fluxes, and very high temperatures. The re-entry phase of the flight trajectory produces the severest conditions as temperatures, heat fluxes, and decelerations are at their maximums. It is these three factors that are responsible for the most significant materials problems. Although it is possible to vary the magnitude of these factors through variations of the flight trajectory, the following typical values are an indication of the severity of the induced environment for various families of glide vehicles. Decelerations may vary between 1 and 50 G's and the hot areas of the vehicles will experience heat fluxes between 50 and 300 BTU/ft²/sec with total heat inputs varying between 10,000 and 400,000 BTU/ft² and maximum temperatures between 2500°F-8000°F (1371°C-4426°C) with associated exposure times of 20 to 60 minutes. The re-entry velocities of the gliders will vary with their mission. Re-entry velocity is approximately 26,000 feet per second from an Earth orbit and 36,000 feet per second from a Lunar mission.

Ballistic Re-entry Body

The ballistic re-entry body under consideration here is the nose cone of the weapon delivery section of an intercontinental ballistic weapon system.

Except for severity, the type of induced environment for a ballistic re-entry body will be similar to that of a glide vehicle. The temperatures and heat fluxes for nose cones will be of significantly higher magnitude with the following typical values; stagnation temperatures of 3800°F-15,000°F (2093-8316°C), on an advanced ablation body stagnation temperatures will probably not exceed 5000°F-6000°F (2760-3316°C). Heat fluxes will vary between 200-4000 BTU/ft²/sec, however, exposure times are much shorter than for a glide vehicle (<1 min). In addition, total heat inputs are less, perhaps one half order of magnitude for the most advanced designs.

Solid Propellant Rocket Motors

Of the material considerations for future solid propellant rocket motors, those of the nozzle are the most challenging and are a direct result of the recent advances in obtaining higher performance propellants to propel the heavier payloads of the advanced systems. The two service environmental parameters generated by these advanced propellants that are responsible for the materials problems are: flame temperatures of 5000°F-8000°F (2760°C-4426°C), and an exhaust gas that is extremely reactive. In addition, the firing durations of the advanced solid propellant rocket motors may extend up to 2 minutes, nearly twice those of present generation motors; because of the metallic additives there may be, depending upon the magnitude of the flame temperatures, an increase in the amount of particulate matter in the exhaust gases, also, associated exhaust velocities may vary from 5000 to over 8000 feet per second.

Design Philosophies

For the re-entry applications (i.e., leading edges, nose cones, wing and body panels), various materials approaches have been suggested and each approach will depend upon the design philosophy chosen to accomplish a given mission, (i.e., ablative, radiative, heat sink, or cooled structure). The refractory inorganic nonmetallics have been suggested as candidate materials for incorporation into most of these thermal protection mechanisms.

The solution of the solid propellant rocket nozzle materials problem will lie in the development of nozzle materials systems. The rocket nozzle materials system has been described as, "a complex of materials, each selected for a particular primary function within the system and each of which, in turn, modifies the environment to which the associated materials are subjected".* This approach has developed since there is no ideal nozzle material and it is synonymous, in principle, to the thermal protection systems of re-entry vehicles.

Basically, the nozzle materials systems will consist of the following elements: a flame barrier (erosion resistant) layer which is exposed to the direct impingement of the exhaust gases; a load bearing member, or shell which is designed to carry the structural or dynamic loads, and an intermediate layer or temperature moderator which could consist of an insulator, conductor, or heat sink material or a combination of the three, so placed as to reduce the heat transfer to the load bearing member.

Although the results of simulated and actual rocket firings that were concerned with describing the potential of ceramics as nozzle inserts were not encouraging, ceramics are one of the classes of candidate materials being considered for use in nozzle materials systems. Their potential, in the main, is the interesting insulative characteristics possessed by certain ceramics, notably the oxides. While other ceramics possess interesting properties, i.e., extremely high melting points, high temperature stability, etc., information is not available which adequately describes their ultimate potential as components of nozzle materials systems.

Research Aims

The potential applicability of the refractory inorganic nonmetallics to the aforementioned re-entry and propulsion protection mechanisms, as well as to other applications, has been indicated in many instances through cursory investigations on materials frequently poorly

* Report MAB-158-M, Vol II, 30 Nov 1959

characterized in terms of impurities, microstructure, process controls, bonding, etc. Through research directed towards obtaining well-characterized materials, along with the substantial property improvements that are expected to result, it will undoubtedly be demonstrated that these materials, by virtue of their other characteristics, possess an increased capability for structural and propulsion applications.

However, whatever the degree of optimism that may prevail by the nature of the improvements resulting through research, the refractory inorganic nonmetallics (ceramics) will probably remain brittle materials. One must therefore obtain a fundamental understanding of the nature of brittle fracture. In addition, it is mandatory that the eventual utilization of ceramics as load bearing members must rely on the establishment of a design technology for brittle materials. The structural designer must possess information that will enable him to incorporate brittle materials in his designs. Although present knowledge is lacking on how to design with brittle materials, it has been proven that if proper consideration is given to brittle material characteristics, through proper design philosophies, reliable structural components are obtained.

It should be quite evident that much remains to be accomplished towards achieving the degree of technology that will permit the utilization of those ceramics and intermetallics that have structural potential, thereby, hastening the solution of many of the materials problems associated with our advanced and future aerospace systems.

Applications and Requirements References

1. WADD Technical Report 60-716, Part I, (U) Materials Requirements for Advanced and Future Air Force Weapon Systems, dated October 1960.
2. Report MAB-151-M, (U) Report on Thermal Protection Systems, dated June 1959.
3. Report MAB-158-M, Standing Review of Department of Defense Materials Research and Development Program, Vol II, dated November 1959.
4. Report MAB-169-M, Report of the Ad Hoc Committee on Refractory Inorganic Non-metallic Structural Materials, dated January 1961.

TABLE I

<u>COMPOUND</u>	<u>MELTING POINT</u>
TiB ₂	> 2600 C (4712F)
ZrB ₂	3000C (5432F)
Nb B ₂	> 3000C (5432F)
TaB and TaB ₂	> 3000 C (5432F)
HfB ₂	3060 C (5540F)
ThB ₂	> 2500 C (4532F)
90% ZrB ₂ , 10% MoSi ₂	> 2360 C (4280F)

TABLE 2
SUMMARY OF INTERMETALLIC COMPOUND PROPERTIES
(as currently available)

	Zr Be ₁₃	Nb Be ₁₂	Ta Be ₁₂	Mo Be ₁₂	Ta ₂ Be ₁₇	Hf ₂ Be ₂₁	Mo Si ₂	Ta Si ₂	W Si ₂
MELTING POINT, °F	3500	3070	3360	3000	3610	>3500	3690	4350	3960
X-RAY DENSITY, g/cc	2.72	2.91	4.18	3.03	5.05	4.26	6.24	9.10	9.87
MAX. TEMP. FOR 10-HOUR SERVICE IN DRY AIR, °F	3000	2900	3000	2900	3000	3000	>3000	>3000	>3200
MODULUS OF RUPTURE, 10 ³ psi									
2300°F	36	39	56	42	67	20	26	29	57
2500°F	36	39	43	30	54	24	28	13	70
2750°F	25	18	26	13	30	17	13	16	51
YOUNG'S MODULUS, 10 ⁶ psi									
2300°F	25	25	24	15	15	28	40	50	50
2500°F	20	15	14	12	11	15	25	35	48
2750°F	10	10	10	1	10	10	12	14	15
THERMAL CONDUCTIVITY BTU hr ⁻¹ ft ⁻² °F									
1600°F	21.0	17.9	11.0	18.2	—	—	18.4	—	—
2600°F	20.8	19.0	10.5	17.5	—	—	—	—	—
SPECIFIC HEAT, BTU/lb °F									
1600°F	0.41	0.40	0.28	0.41	—	—	—	—	—
2600°F	0.46	0.43	0.30	0.45	—	—	—	—	—
THERMAL EXPANSION, 70 - 2600 °F 10 ⁻⁶ in./in. °F	9.8	9.2	8.3	—	8.57	9.05	4.80	4.67	4.4

TABLE 3

OXIDATION DATA FOR SELECTED INTERMETALLIC COMPOUNDS

COMPOUND	PERCENT OF ABSOLUTE DENSITY	TEST TEMPERATURE °F	WEIGHT GAIN (mg/cm ²)			MILS - PENETRATION	
			1 HOUR	5 HOURS	10 HOURS	MEASURED	CALCULATED
TaBe ₁₂	98.9	2900	1.9	3.9	5.9	0.2	0.7
TaBe ₁₂	97.8	3000	11.3	25.4	36.6	3.1	4.3
Ta ₂ Be ₁₇	98.8	2900	2.6	8.4	16.5	0.7	1.9
Ta ₂ Be ₁₇	99.6	3000	7.9	15.2	33.0	1.9	3.8
Hf ₂ Be ₂₁	94.7	2900	1.5	3.7	4.8	<1.4	0.6
Hf ₂ Be ₂₁	100.	3000	13.1	32.5	59.1	—	7.6
Hf ₂ Be ₁₇	88.2	2900	7.8	10.2	14.3	<2.8	1.8
Hf ₂ Be ₁₇	88.5	3000	9.7	21.2	31.9	5.2	4.1
TaSi ₂	96.3	2900	0.8	1.4	1.4	<0.7	0.1
TaSi ₂	99.8	3000	0.9	1.6	2.4	0.1	0.3
WSi ₂	98.7	2900	(-0.5)	(-0.4)	(-0.3)	<0.8	—
WSi ₂	98.8	3000	0.2	1.7	1.9	0.5	0.2
MoSi ₂	94.9	2900	0.7	0.8	1.0	0.3	0.1

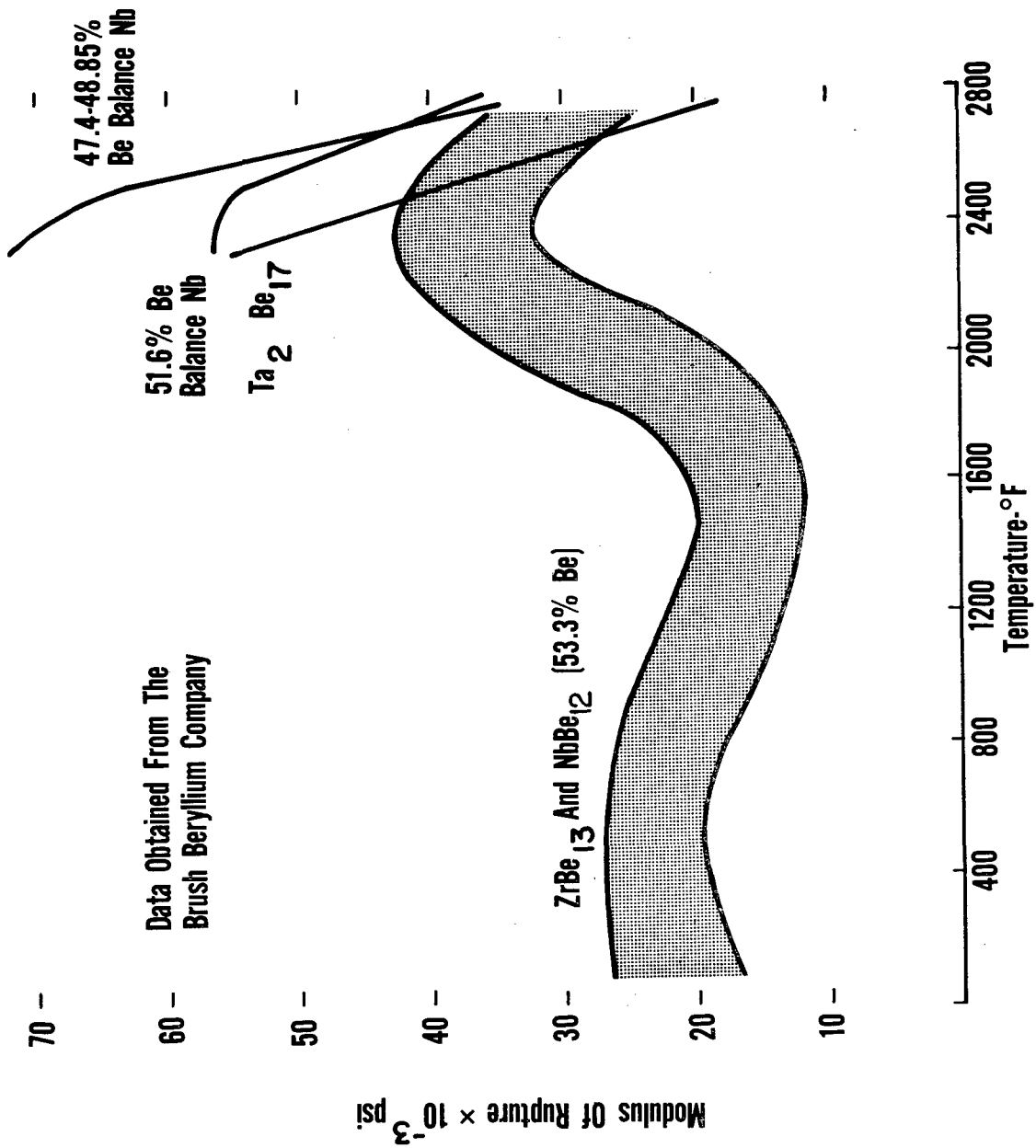


Figure 1. Mechanical Property Trends

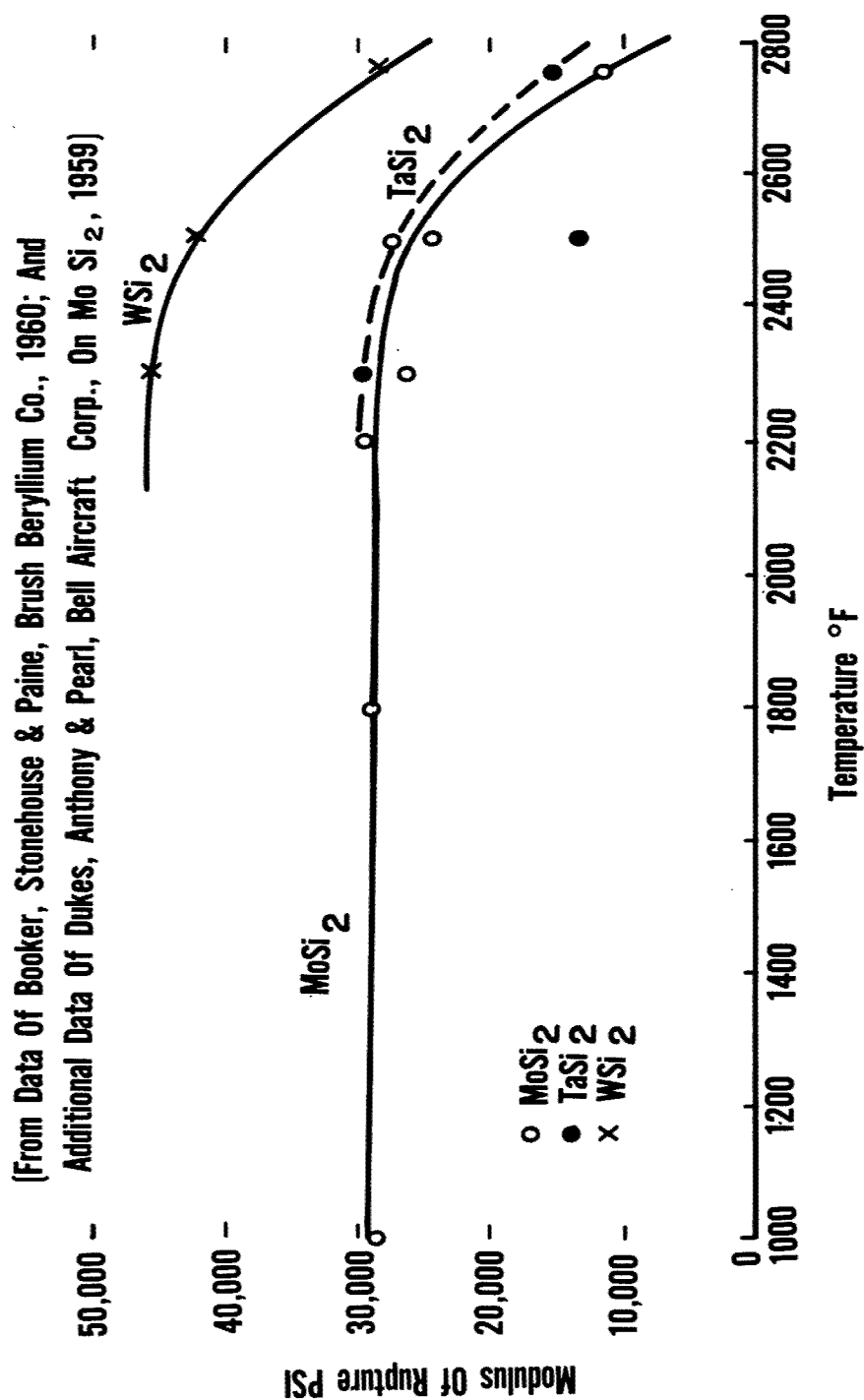


Figure 2. Oxidation Test Data

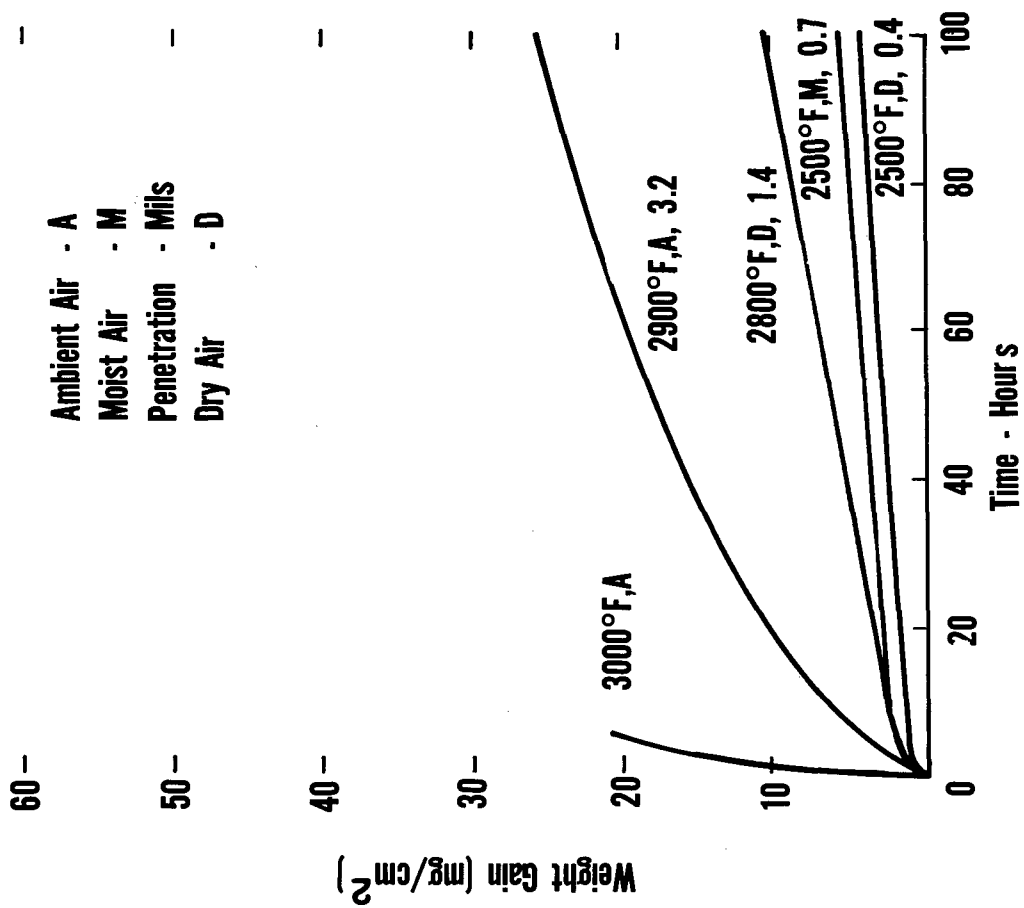


Figure 3. Modulus of Rupture vs. Temperature for Silicides

FIBROUS MATERIALS

Chairman

Mr. C. A. Willis

Speaker

Mr. J. H. Ross

Panel Members

Mr. L. G. Picklesimer

Capt E. L. McLeod

Dr. A. M. Lovelace

ORGANIC AND INORGANIC FIBROUS MATERIALS

J.H. Ross

Directorate of Materials and Processes, ASD

The past role of fibrous materials in the protection of man and his accouterments from environments encountered in an oxygen rich atmosphere are well known. This was accomplished by employing commercially available fibers to fulfill overall Air Force requirements which effectively limited research to overcoming such unique requirements as abrasion, chemical deterioration, shock loading and flash thermal, to name a few. The role of fibrous materials in the space age, of necessity precludes such an approach.

In the early stages of the space age which began with the firing of instrument packages to the extreme outer edge of our atmosphere, the first deficiency of commercial fibers became apparent. (figure 1) (Melted Ribbon Chute). The poor resistance of nylon to elevated temperatures resulted in the melting of the materials at 482°F. Concurrently, high shock loads, imposed by deployment of decelerators at super and hypersonic speeds, have been extremely detrimental to fibrous materials. (figure 2) (Shredded Ribbon Chute). This damage resulting from deployment at Mach 3 at 60,000 ft. altitude, was caused by high stresses imposed on the horizontal members. These stresses are a combination of tension and high frequency flutter or vibration.

As the Air Force continues probing into the extremes of space, fibrous materials used must be capable of functioning under the hyper environments that future aerospace systems will encounter. The flexible fibrous materials will be utilized as deceleration devices for aerospace vehicles (including re-entry), instrument and capsule recovery. The need for light weight but large volumes for aerospace systems has pointed up acceleration of research in the area of materials for expandable structures. The advantage of inflatable structures include facility of compaction and subsequent ease of expansion upon achievement of operational altitude.

Flexible fibrous materials will also be required where high strength is needed as a substrate for elastomeric coatings to be utilized in tires, fuel containers, diaphragms and ducting which must withstand unusual environmental conditions of temperature and pressure while under load and continuous flexing. Further uses of these fibrous materials include thermal insulation and, because of inherently high strength to weight ratios, rigid structures by means of fiber reinforcements for plastic and other composite materials. Figure 3 covers a broader spectrum of planned uses.

The utilization of unique systems composed of fibrous materials in aerospace environment will necessitate ability to withstand structural loading, cryogenic temperatures, micrometeoritic bombardment, aerodynamic re-entry heating, vacuum and solar radiation, abrasion, and repeated or cyclic flexing. In analyzing the referenced environments as related to presently available fibers, it can be shown that present fibers will fail to withstand one, or more of these environments. For example:

1. Nylon has the strength, flexibility, abrasion resistance, and energy absorbing capability desired, but is unusable above 300°F.

2. Fiberglass has the strength, and ability to resist temperatures up to about 800°F, but has extremely poor abrasion resistance, cannot be flexed, and due to low elongation has poor energy absorbing characteristics.

Analysis of known and anticipated requirements for fibrous materials can best be summed up generally in figure 4 and specifically in figure 5. Other requirements must be considered which include the ability of coated fibrous structures to rigidize upon loss of plasticizer, time to rigidize at specific levels of low density, and resistance to cryogenic temperatures during and after rigidization, and fabricability.

Strength and temperature resistance are the most important requirements for fibrous materials. However, a review of the overall requirements reveals that flexibility is a critical factor. Especially so, when it becomes apparent that fibers with high strength at elevated temperatures have a high modulus and quite a bit of stiffness. Figure 6 shows the Modulus, (E) for various materials as well as the fiber diameter necessary to achieve the equivalent flexibility of nylon. An indication of good flexibility is evidenced in fibers which have good knot strength. For fibers to have good knot strength, they must have a clearly defined yield region (on the stress-strain curve), in order to permit redistribution of the stresses to the lowest possible levels; they should also have a high ultimate tensile strength, since glasses, ceramics, and refractory metals are poor in flexibility; progress toward their usage will undoubtedly be slow. This becomes more evident when we review the present fibrous materials applied research program.

Basically, this research program is divided into three broad areas:

1. Fiber Drawing and Modification
2. Fibrous Structural Materials, and
3. Coatings for Fibers and Fibrous Materials.

These areas are of sufficient depth to prevent the overlooking of any approach which might lead us to the desired goal. Considering this, all basic types of materials-organic, ceramic and metallic are included in the fiber research program.

Research programs in the area of new fiber achievement is concentrated in forming of fibers from new polymers, impregnating organic polymers with metallic oxides and drawing of metal fibers.

The practice of spinning inorganic fibers from a melt suffers from serious disadvantages when extremely high melting inorganic materials are used. The materials must be handled at extremely high temperatures and are often corrosive. Spinning equipment is not available for handling such melts and the development of such equipment will be extremely difficult. As a result of research efforts, a technique has been found to bypass the problem of equipment to handle batches of molten materials. The method consists of spinning an organic fiber at room temperature, which contains a large percentage of inorganic components (Oxides). The composite fiber is then sintered to remove the organic portion of the fiber and form the inorganic fiber. The organic polymer employed must meet the following criteria: 1. Must form strong flexible fibers. 2. Must char without melting, at a temperature high enough that an inorganic liquid phase will form. 3. It must burn out completely, leaving no carbonaceous residue.

The inorganic constituents employed must meet the following criteria: 1. A small amount of inorganic liquid must form at temperatures low enough to be present before charring of the organic material is complete; 2. At all stages after the start of charring there must be an inorganic liquid phase of high viscosity and surface tension; 3. The liquid phase must be controlled in order to maintain a fibrous form; 4. The particle size must be controlled according to the desired size of the finished fibers.

Composite fibers have been produced that contain 80 percent by weight of inorganic material in poly-acrylonitrile. These composite fibers were then heat treated to raise the decomposition temperature of the poly-acrylonitrile. After heat treating, the composite fibers are charred at 400°C and the residual carbon removed at 1000°C to produce a completely inorganic fiber. Inorganic fibers several feet in length and 100 microns in diameter have been produced in this way.

Problems still to be solved are the use of more refractory inorganic materials, diameter, crystallinity, and achieving flexibility in the fibers formed; the latter is related to diameter. Most of the operations of the spinning method are carried out at room temperature in a fairly straight forward manner; only a minor portion of the operation is high temperature.

Organic fibrous materials in use at present have very definite limitations on their capabilities to resist high temperatures, ultraviolet light and other environmental extremes. Additives have been widely used with only marginal improvements.

In the search for high temperature organic fibers, difficulties are encountered in forming fibers from the high melting material. Fibers are generally formed by one of three methods: melt, coagulation, or solvent spinning. With melt spinning the polymer often decomposes rather than melt at the molecular weights required for fiber formation. In solvent and solution spinning the polymer, finding a suitable solvent or system of solvents is the difficulty.

Research is being conducted to form polymers which contain residual unsaturation; thus the molecular weight can be increased by affecting crosslinking after the formation of the fiber.

Continual screening of industry's research is carried on. An example of this effort is the studies of HT-1. Since it has been brought to our attention considerable effort has been expended toward defining the fiber's characteristics. Its resistance to gamma radiation has been found to be far superior to nylon (figure 7). Under certain conditions gamma radiation and heat caused cross-linking resulting in increased strength. (figure 8). HT-1 has excellent strength retention, if properly treated, at temperatures up to 600°F. (figure 9). Its non-melt, non-fuse characteristics, coupled with toughness superior to nylon cannot be overlooked for decelerators, and related fibrous structures.

As RT-1 is being proven, another polymer capable of being drawn has been discovered. From the polybenzimidazole family, this fiber is spun from a solution of dimethyl sulfoxide and has been evaluated with promising results for high temperature applications. The fiber had a tenacity of 3.93 grams/denier approximately 6.8 percent elongation and modulus of elasticity of 2.2×10^6 psi based on a 8 denier fiber. The fiber retained structural integrity after exposure to 977°F. Further studies of techniques to increase the molecular weight, achieve greater orientation, crystallinity, and subsequently higher strength, are being conducted.

Polymeric materials are susceptible to damage by various types of radiant energy. Ultraviolet light is an example of radiant energy which causes extensive damage to polymers used in fibrous materials. Since a considerable portion of the most energetic ultraviolet light is screened from the earth by the atmosphere, much more severe damage can be expected in a space environment. Research has shown that properties of fibers such as elongation, tensile strength, Young's modulus, and the molecular weight of the polymer are decreased after relatively short exposure to ultraviolet radiation. As was predicted damage was more severe at the shorter wave lengths. At 375 mμ there was no damage since the energy at this wave length corresponds to the energy of the carbon-to-carbon bond.

In the deterioration there are two competing reactions: chain scission and cross-linking. The environment seems to have considerable influence as to which reaction dominates. In an inert atmosphere such as nitrogen, chain scission is the dominant reaction. The effects of orientation of molecular chains in the fiber on deterioration are being investigated. The effect of the presence of oxygen in the ambient atmosphere is also being studied. Polymers that have been investigated to date are nylon, poly-acrylonitrile, polyethylene-terephthalate, polyethylene, and polytetrafluoroethylene. Evidence shows that the dominance of chain scission in nitrogen is due to pressure effects rather than to the atmosphere. The nitrogen present tends to retain hydrogen which has been split off from the polymer and thus promote chain scission over crosslinking.

The utilization of metal fibers in various high temperature flexible structures poses problems seldom encountered or experienced with organic type fibers. For high temperature use, oxidation, abrasion, and flexibility must be considered, since these can seriously affect the operating capability of fine metallic fibers. Therefore, the metal whether it be pure or an alloy is of concern. A number of factors have had to be considered in choosing a metal for study. These factors are: 1. Oxidation resistance at temperatures of plus 1500°F; 2. Strength at high temperature; 3. Ductility or elongation; 4. Drawability.

From the beginning it was apparent that most pure metals could not be utilized due to inherent low strength, however, certain of the refractory metals have excellent strength properties, are easily drawn to diameters of 0.4 mil and still retain some ductility. The refractory metals have high melting points and good high temperature strengths. A problem to overcome making use of them is the resolution of their extremely low oxidation resistance. The refractory metals of most interest are Molybdenum and Tungsten. Although the tensile strength of Molybdenum is not as good at high temperatures as Tungsten, its lower density 10.28 g/cc to 19.3 g/cc makes it a more interesting material. Figure 10 shows the tensile properties of Molybdenum and how drawing it results in increasing tensile strength as diameter is decreased. To overcome the problem of oxidation, our research is being aimed at protective coatings. Many methods of applying coatings exist, and electrodeposition is the most promising.

Some of these studies have been concerned with gold plated moly and tungsten utilizing in addition platings of palladium, rhodium, chromium and nickel. Oxidation tests are conducted by hanging a loose coil of fiber in the center of a furnace at 2000°F. Preliminary results show that gold is unsatisfactory, due to the rapid diffusion of the molten gold into the refractory metal. Using a 2-mil Moly as a base, a 0.1-mil coating of nickel was applied, followed by 0.05-mils of chromium. The chromium plating was diffused into the nickel coating. After exposure to 2000°F for 60 seconds, the fiber had a tensile strength of 158,000 psi. In addition, thin electrodeposits of nickel and chromium, electrodeless nickel and combinations of these have been added to 1-mil Moly. In all cases, the

electro-plated fibers were heated in argon for 5 minutes at 2000°F, to diffuse the nickel and chromium so as to form a more oxidation resistance coating and to improve the adherence of the coating to the Moly. Tests have shown that the electroless nickel affords much better protection in combination with chromium. Although the melting point of electroless nickel is only 1635°F, it alone will provide some protection to Moly fibers at 2000°F up to 3 minutes in air. It is probable that the thin coating alloys very quickly with the moly at 2000°F and prevents catastrophic oxidation. These coatings will be applied to basic refractory fibers as fine as 0.4-mil dia., to achieve a final diameter of 0.5 mil or less. It must be noted that even though anticipated usage of these metals would be in a low density atmosphere, the oxidation studies are conducted at ground level densities. Considering the velocity of satellites in orbital flight, and during re-entry, even in hard vacuum environment, oxygen concentrations will build up, necessitating the simulation of such critical conditions.

Another class of metals the high temperature alloys or "Super Alloys" are worthy of consideration in the quest for high temperature fibers. There is sufficient data on fully heat treated sheet material rolled from some of these alloys (figure 11) to indicate that they have sufficient tensile strength at elevated temperatures to attempt drawing them into fine fibers. With respect to the oxidation characteristics, it is known for example that certain iron alloys form a dense adherent oxide layer when exposed to air which creates extreme oxidation resistance. However, the tensile strength of most iron alloys falls below 20,000 psi as the temperature reaches 1500°F and efforts to increase the tensile strength have not been too successful.

The nickel alloys on the other hand exhibit good oxidation resistance while retaining a good percentage of strength after exposure to 1500°F. The present research program on metal fibers include two nickel alloys—Rene 41 and Inconel 702. The excellent original tensile strength of the nickel alloys as represented by Rene 41 (figure 12) combined with good oxidation resistance, explains our reasoning in conducting research toward the fine fibers of this alloy.

Similarly, cobalt can be alloyed so that the oxidation resistance is of the same magnitude as the better nickel alloys. Studies are concentrated on fibers produced from Elgiloy. To a certain degree Elgiloy and Rene 41 are quite similar. Similarity exists in specific gravity (8.25 to 8.3), Elongation (17.5 percent to 17 percent) and Tensile Strength (225,000 psi to 286,000 at 0.5 mil). Their compositions are shown in figure 13. Fibers of 5,2,1, and 0.5-mil diameter have been drawn for utilization in our research studies. Primary studies are being conducted to determine the oxidation resistance, tensile strength and elongation after exposure to 1500, 1800 and 2000°F, for 1.5 and 10 minutes. These studies to date on Elgiloy and Rene 41 have revealed that: 1. Oxidation rate decreases with decreasing diameter in the range of 5 to 0.5-mil fibers. 2. Percent area reduction due to oxidation increased with decreasing diameter, and 3. Oxidation decreased the total cross sectional area by less than 4 percent (figure 14).

A comparison of the tensile strength (figure 15) of these alloys after exposure to 1500, 1800, and 2000°F for 1, 5 and 10 minutes reveals, at 1500°F the Rene 41 is superior, but as the temperature increases the Elgiloy retains the larger percentage of tensile strength. Even more significant than the loss in strength has been the reduction in room temperature ductility after oxidation. Losses of as much as 90 percent have been noted for the specimens exposed at 2000°F for 10 minutes. The loss is much greater for the Rene 41 fiber (in diameters of less than 2 mils) than for the Elgiloy.

The fact that a metal is resistant to temperatures and has high original and at temperature tensile strength is not the only indication of its fiber forming ability. The metal must be capable of being drawn to the diameter most satisfactory for use in flexible fibrous materials. Normal practice today is to reduce the diameter of a metal gradually, starting with a bar and through intermittent drawing, annealing and coldworking, achieving an extremely fine fiber. In the case of refractory metals and super alloys the last drawing operation utilizes diamond dies to achieve roundness and consistency of product. This approach is extremely expensive and time consuming. New techniques are being considered, which could result in fine fibers at relatively low costs. These approaches include 1. Drawing from a melt. 2. Drawing over hot pins. 3. Drawing bundles of wires through a single die. 4. Etching by Electrolysis. Included in this phase of research, are studies on the techniques for gathering and bundling fine metal fibers, to achieve multifilament yarns capable of being woven. Present studies in stranding of 1/2-mil fibers of super alloys have resulted in strands of 50 filaments in such combinations as 7/7/1, 5/10/1, 10/5/1. Translation of fiber strength to yarn strength is of prime concern in continuous filament yarns with the goal 100 percent translation. In the case of these fibers the strength achieved in the first yarn was 1.47 lbs. and the second was 1.46 lbs. The 1/2-mil fiber had a strength of .0288 lbs. Roughly all of the fiber strength was therefore retained in the plied yarn.

A brief summary of the status of our fiber research is graphically presented in figure 16.

It might be pointed out that the obvious advantages of fibers for flexible, pure tensile loaded materials has received by far the greatest amount of attention. For more rigid applications, the substantial increase in load carrying efficiency realized through fiber formation has been exploited for the most part only as so called "reinforcements" with other types of materials. It is believed that much could be accomplished with new and refined means of fiber assembly into highly efficient flexible structural members.

Our research on fibrous structures is slanted toward the affecting of optimum low or zero porosity materials for decelerators and other devices that could advantageously be fabricated from fibers which are resistant to temperatures up to 2000°F. In the case of high temperature resistant fibers such as the super alloys, their density is of such a magnitude to preclude achieving a high strength to weight ratio solely with metals. Consideration must be given to techniques for achieving low controlled or zero porosity, such as: 1. Single Fiber Coatings; 2. Yarn Coatings; 3. Flexible Fibrous Structure Coatings; 4. Yarn Blending.

In reviewing these four areas, it became apparent that applying coatings to the individual fibers of a yarn bundle is of a challenging nature. The ability to diffuse coatings through fiber bundles can be difficult especially where consistency of coating thickness is desired. The only possible use of this type coating can be made when the coating is applied as the fibers are drawn and before gathering, as in the case of glass or ceramic fibers. A very good example of this latter approach is our work with fused silica yarn and fibers. Using as a base, a fused silica yarn, various finishes or coatings ranging from silicone oils through various oxides which can be deposited as thin films have been studied. Most successful to date has been magnesium acetate. Tensile tests have shown that fibers removed from treated yarns were equivalent to fibers from unfinished yarns exposed to 1000°F for 16 hours. Abrasion resistance has been improved by a factor of 2. These fibers were treated at the bushing prior to gathering into a bundle.

The step to yarn coating, could open many new fields with respect to achieving yarns which have strength, and when woven have greater flexibility and abrasion resistance. As far back as 1956, we studied the effect of coating glass yarns prior to weaving (3). This study revealed that teflon coated glass yarns could be woven to give a controlled porosity flexible structure, capable of withstanding flexing and abrasion on itself, yet capable of use at temperatures to 700°F. The use of chemical and mechanical treatments for enhancing flexibility and abrasion resistance is now being studied using glass yarns. Concerning chemical treatments those referenced for fibers as well as certain silicone finishes have been found to be most satisfactory. Tape samples having silicone (XET-4327) added, retained a greater percent of strength after being compressed under 250 psi, at 500°F, (this was a specific unfulfilled requirement). Another area of chemical treatment involved converting the flexible yarn to a rigid bundle when exposing it to the environment of outer space. By using treated yarns (prior to weaving) and then coating the woven structure, maximum rigidity and impermeability with a minimum of weight, was possible. Chemical systems being used include the urethanes and vinyls. By careful selection of the plasticizing compound, rigidization can be effected in a hard vacuum using the vapor pressure generated for inflating the structure. The use of this type fibrous material for antennas, and solar collectors in space could open an entirely new concept in exploration. Mechanical treatments for the yarns involve techniques such as texturizing. This type yarn has loose ends or loops protruding from its surface; these offer advantages in the rigidization, including high resistance to internal shear forces.

Use of texturized yarns in fibrous structures can increase adhesion of coatings and add structure flexibility prior to rigidization. In coating the woven structure, the ideal approach would be to fill only the interstices or openings between the yarns, however this has not yet been successfully accomplished. Processes such as knife coating, dip coating, and flame spraying are being investigated. The use of flake or frit added to the woven structure as flock or to a coating can effectively increase elevated temperature resistance.

One of the most practical approaches to achieve low porosity structures is the utilization of yarns composed of more than one fiber. The use of a high strength, temperature resistant metal wrapped with a staple yarn composed of a flame proofed cellulosic, acrylic fiber, or wool would effectively create a yarn array having a good cover factor. The staple fibers would increase coating adhesion and their low density, generally less than 2, would result in lower weight structures. Actual blends composed of Elgiloy and wool are being prepared and will be woven into structures. Flexibility, determination of repeated stressing characteristics at high temperatures, in addition to tensile and energy absorption will be obtained on these blended fiber structures. The inclusion of new high temperature organic fibers such as HT-1, or PBI could effectively create an ablative type structure for use in leading edges, nose cones, and re-entry bodies.

In the area of inflated or expandable structures, consideration must be given to the woven structures used for protecting man in the low density or vacuum environment of space. Materials used in space suits must when pressurized, remain dimensionally stable, and yet be flexible enough to permit body movements. This presents a design problem because the materials which are rigid enough to provide dimensional stability are not flexible, and materials which are extensible enough to flex do not remain dimensionally stable.

The two requirements cannot be compromised but must be resolved by special techniques by making "structures" that have both characteristics. If these "structures" are not air tight, as in the case of fabrics, they must be placed over some type of bladder which will retain the air. Bending flexibility has been solved by two different design

principles. The first one utilizes a cylinder constructed from a one-way stretch material that is restrained from stretching by longitudinal cords placed at the cylinder sides (figure 17). Since these cords are on the cylinder sides, they do not interfere with bending flexibility. The material used in this method can be either bellows, one-way stretch fabric, or even a fibrous material cylinder with large longitudinal wrinkles.

The second method consists of taking a loose material, (a net for example) and placing it in the shape of a joint in such a way that it will not change its dimensions when pressure is applied. (figure 18). This can be done by calculating or measuring the equilibrium geometry at the desired pressurization and then setting the structure initially at that geometry. If the structure starts out at its equilibrium geometry, it will not change shape when pressure is applied. However, since the fibrous material is loose it can still allow extensions to take place; and therefore the cylinder can bend. The difficulty of bending will depend upon the type of fabric.

In the design studies, mathematical and experimental work was done. Many fibrous structures have been designed, analyzed, and evaluated as pressurized cylinders. The aim is always to minimize bending moments, and the tendency to spring back to the original position. Present research consists of extending some of the useful results found for cylinders into the more complicated shapes that are required in a space suit. In addition, several new types of fibrous structures are under study for use in cylindrical joints.

The fabrication of expandable structures such as re-entry lifting surfaces and space-stations necessitates new coated fibrous structures impermeable to gas penetration, with sea level pressure on one side and vacuums as low as 10^{-9} mm Hg on the other side, ability to withstand re-entry temperatures to 1500°F for time cycles of 10 minutes. But basically these are requirements shown at the beginning of this presentation, as are other requirements for expandable structures. However problem areas exist which must be resolved to achieve optimum fibrous structures. These areas include: 1. Yarn and structure construction to attain optimum strength and flexibility; 2. High temperature coatings capable of gas impermeability and retaining flexibility up to 1500°F; 3. Techniques for joining high temperature fibrous structures without affecting flexibility, in both uncoated and coated conditions; 4. Ability to resist cryogenic temperatures.

It is difficult to conclude a presentation of this type because each month new advances are made in fibrous materials in our research programs. Each advance seems to indicate the next step to be taken to achieve optimum fibrous material. This has been clearly shown in the case of metal fibers. Two years ago 1/2-mil fibers of Rene 41 and Elgiloy were unknown. With their conception, forming of multi-filament yarns become a possibility. Now that yarns of this type are becoming a fact, construction of the optimum fibrous material for specific space systems will follow. New challenges arise which must be met, new techniques must be proven, and requirements must be fulfilled so that aerospace systems can successfully accomplish their anticipated and required missions.

REFERENCES

1. "Candidate Materials for High Temperature Fabrics", WADC TR 59-155, Sept. 1959.
2. Hamburger, Walter J., "A Technology for the Analysis Design and Use of Textile Structures as Engineering Materials", Edgar Marburg Lecture, 1955, A.S.T.M.
3. "Development of Heat Resistant Glass Textile for Parachute Applications", Contract AF 33(600)-29002, Coast Mfg. Co.

BIBLIOGRAPHY

1. WADD TN 60-299, "Thermal and Gamma Radiation Behavior of a New High Temperature Fiber", 1961, Capt. C.O. Little, Jr.
2. WADD TN 60-298, "Elevated Temperature Behavior of Fibers", 1961, Stanley Schulman.
3. WADD TR 60-897, "The Theoretical Behavior of a Knitted Fabric Subjected to Biaxial Stresses", 1961, 1/Lt. P. Popper, USAF.
4. WADD TR 60-510, "Deterioration of Textile Materials by Ultra-Violet Light", Oct. 1960.

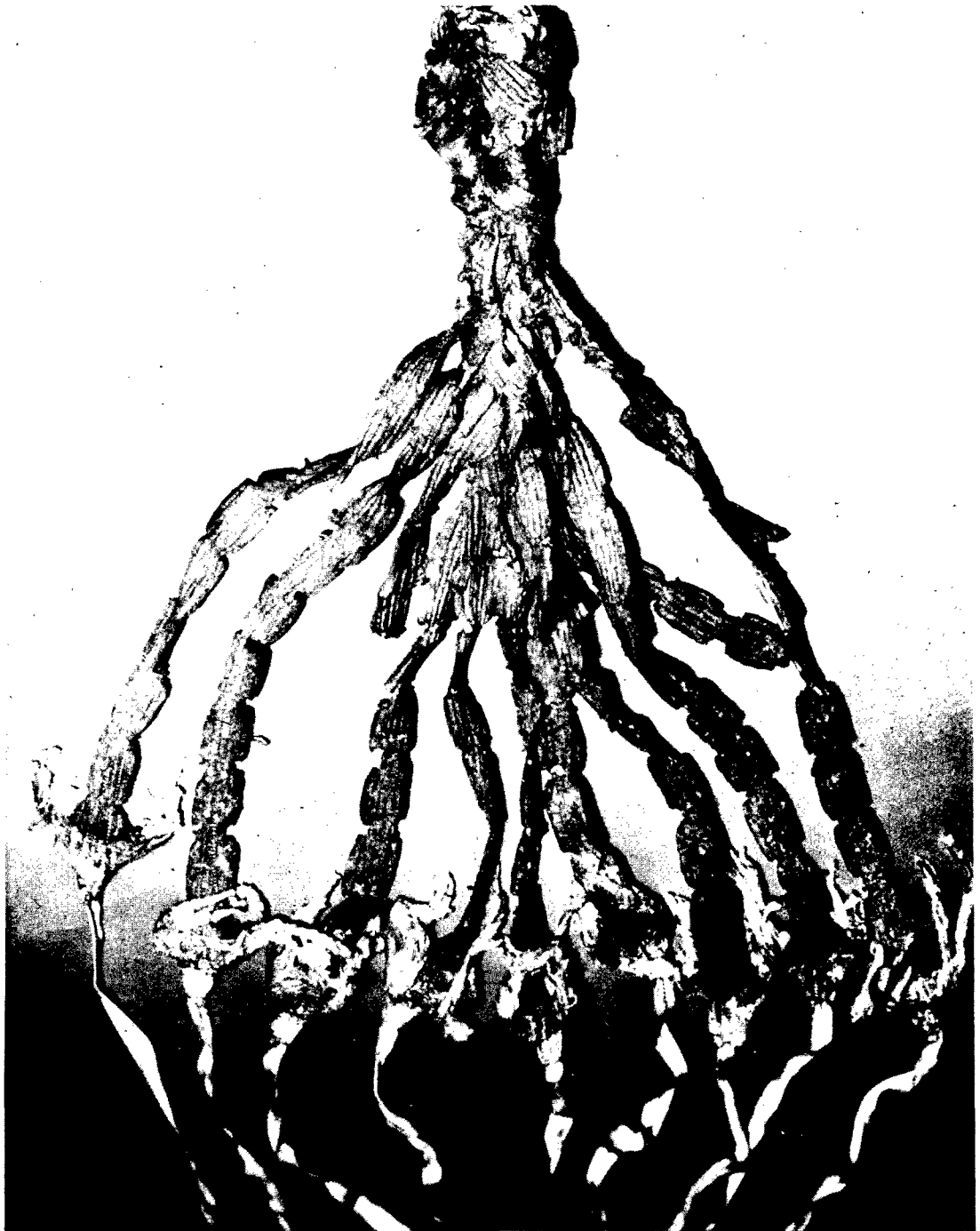


Figure 1.

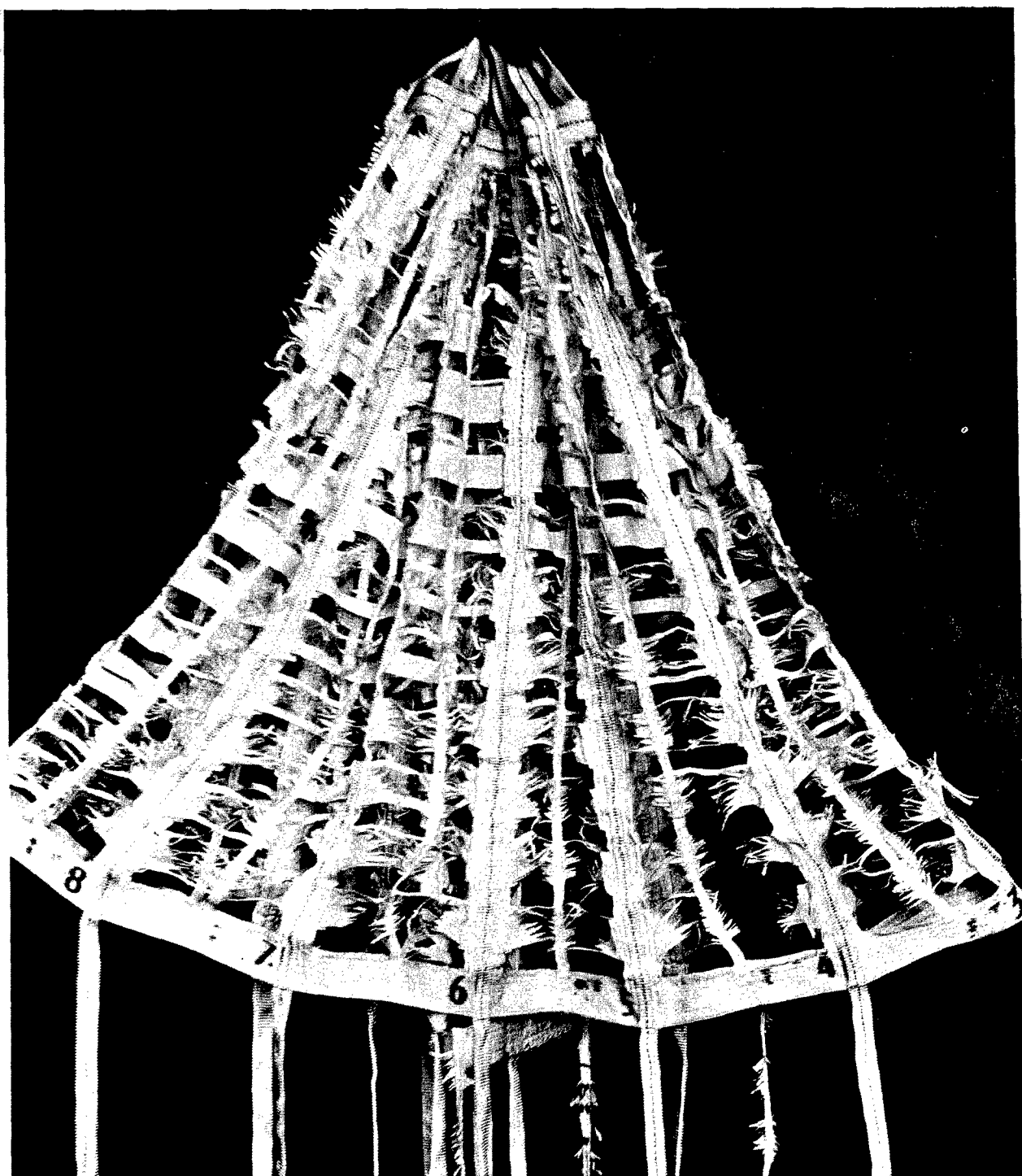


Figure 2.

USES FOR FIBROUS MATERIALS

DECELERATORS

Aero Space Vehicles
Instrumentation Recovery
Terminus Approach Control
Reentry Of Space Vehicles
Capsular Delivery

INFLATABLE STRUCTURES

Energy Collectors
Reflectors And Communication)
Dissipators
Station Protection
Satellites
Re-entry Vehicles
Targets

} For Space Systems

INSULATION MATERIALS

Electro Magnetic Radiation Ranges
Mechanical-Shock, Vibration
Accoustical
Thermal

PRESSURIZED CONTAINMENT

Fluid Storage
Pressure Suits
Tires

RIGID STRUCTURES

Composites
Laminates
Satellites

FIBER OPTICS

Instrument Review
Area Scanning
Remote Photography

PROTECTIVE COVERING

Hyper Environment
Thermal Radiation
Weathering

Figure 3.

PROPERTIES of INTEREST

- **Compatibility With Associated Materials And Treatments**
- **Surface Characteristics**
- **Configuration Control**
- **Flexibility Or Rigidity**
- **Stability To Radiation**
- **Fatigue Resistance**
- **Energy Absorption**
- **Chemical Stability**
- **Heat Resistance**
- **Permeability**
- **High Strength**
- **Bulk**

Figure 4.

TARGET REQUIREMENTS

Temperature	75%	2,000°F For Max. Of 10 Min. 1,500°F For 10-20 Min.
Vacuum And Solar Radiation	80% Strength Retention	Continuous Or Intermittent Exposure Totalling 4×10^7 Langleys At Orbital Altitude
Flexibility	No Failure	Crease Flexing And Compressive Creasing In Cycles For 24 Hours
Compaction	90% Strength Retention	Packing Pressure Up To 150-250 lbs/sq. in.
Vapor Permeability	Impermeable	Inflated With Air Or Helium In An Atmosphere Of Complete Vacuum At 1,200°F
Chemical Resistance	Inert Or Non-Corrosive	Ozone (11 P/M 100 M FT) Ionized Gases
Meteorites	No Penetration	Micro Meteorite Bombardment

Figure 5.

FILAMENT DIAMETERS REQUIRED TO GIVE EQUIVALENT FLEXIBILITY AS NYLON

MATERIAL	M O D U L U S (p.s.i. $\times 10^{-6}$)	DIA. REQUIRED for SAME FLEX- IBILITY 19 μ NYLON (Microns)
NYLON	0.4	19.0
CARBON	0.7	16.8
FIBERGLASS	8.0	9.1
FUSED SILICA	10.0	8.6
COLUMBIUM	22.7	7.1
IRON, NICKEL	30.0	6.6
TUNGSTEN, MOLY.	50.0	5.8

Figure 6.

RESULTS of GAMMA RADIATION

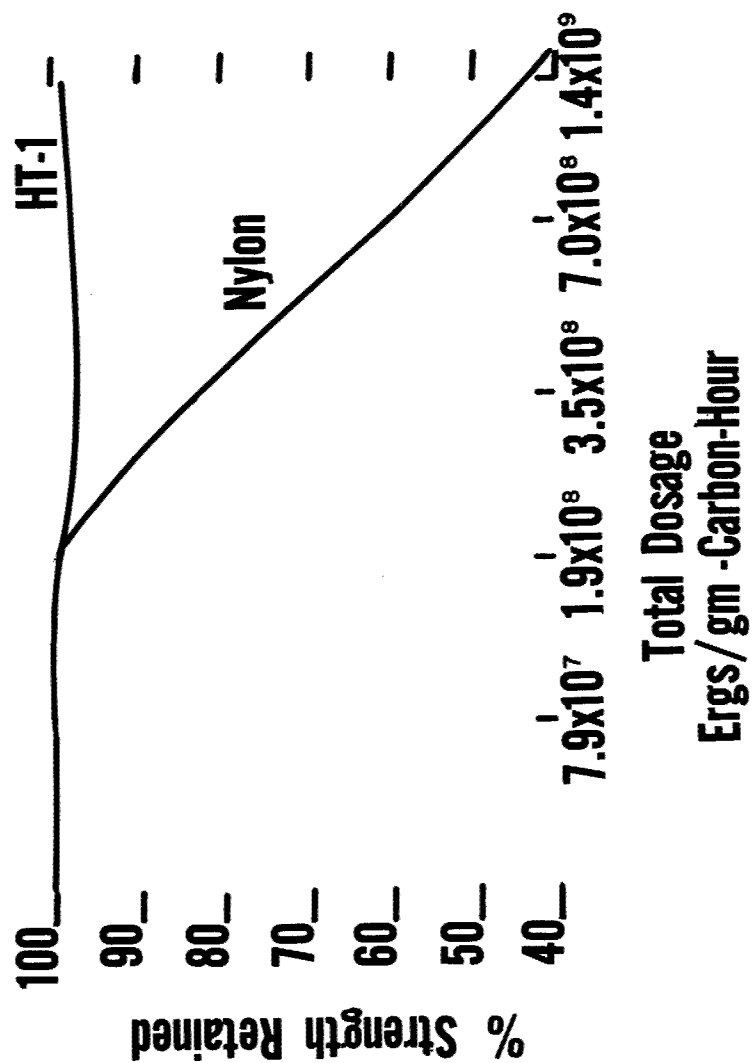


Figure 7.

TEMPERATURE RESISTANCE of HT-1 ENHANCED BY RESEARCH

	Conditions	% Of Original Strength Retained
400°F	Strength Determined While At Temperature	70.7
400°F	Sample Properly Crosslinked Using Heat & Gamma Radiation- Then Strength Determined At Temperature	98.1
400°F	Sample Properly Crosslinked. Oven Aged @ 400°F For 9 hrs. 36 min. Then Strength Determined At Temperature	96.6

Figure 8.

BREAKING STRENGTH DATA of HT-1

Conditions

1. Subjected Simultaneously To Gamma Radiation Plus 400°F.
(Tot.Dosage- 1.4×10^9 Ergs/gm -Carbon-Hr)
- 2.Oven Aged At Indicated Temp.
For 8 Hours.

Oven Aged At Indicated
Temperatures For 8 Hrs.

% Of Original Strength Retained

400°F	96.3	96.3
500°F	85.1	89.5
600°F	58.6	78.2

Figure 9.

Tensile Strength Of Pure Molybdenum

<i>Dia. of Wire—Mils</i>	<i>Tensile Strength—PSI</i>
48—AS DRAWN	14.0—20.0 X 10 ⁴
10—AS DRAWN	20.0—30.0 X 10 ⁴
48—ANNEALED	10.0—17.0 X 10 ⁴
10—ANNEALED	9.0—21.0 X 10 ⁴
5—ANNEALED	20.0—26.0 X 10 ⁴
2.8—ANNEALED	23.0—27.0 X 10 ⁴
1.2—ANNEALED	27.0—32.0 X 10 ⁴

Figure 10.

STRENGTH VALUES of ALLOYS at ELEVATED TEMPERATURES

A L L O Y	SHORT TIME TENSILE STRENGTH (10^3 p.s.i.)		
	1,000°F	1,500°F	2,000°F
STAINLESS STEEL 310 321	67 61	42 (1400) 28 (1400)	11 5
COBALT BASE L-605 N-155	100 90	45 58 (1400)	— —
NICKEL BASE HASTALLOY X RENE'41	94 180	63 (1400) 110	21 40

Figure 11.

Effect of Wire Diameter On Tensile Strength & Elongation

Dia. of Wire - Mils	Tensile Strength - PSI	Elongation - %
10	18×10^4	33
8	20×10^4	27
5	21.4×10^4	24
4	21.6×10^4	24
3	22.8×10^4	19
1.5	25.6×10^4	16
0.5	28.6×10^4	17

Figure 12.

NOMINAL COMPOSITION of ALLOY WIRES

	WEIGHT %	
	RENE'41	ELGILOY
Nickel	55.31 (Bal.)	15.0
Cobalt	11.0	40.0
Chromium	19.0	20.0
Molybdenum	10.0	7.0
Iron	--	15.81 (Bal.)
Titanium	3.1	--
Manganese	--	2.0
Aluminum	1.5	--
Beryllium	--	0.04
Carbon	0.09	0.15
Specific Gravity, gm./cu. cm.	8.25	8.3

Figure 13.

COMPARISON of OXIDATION RATE of 0.5 MIL DIAMETER ALLOYS

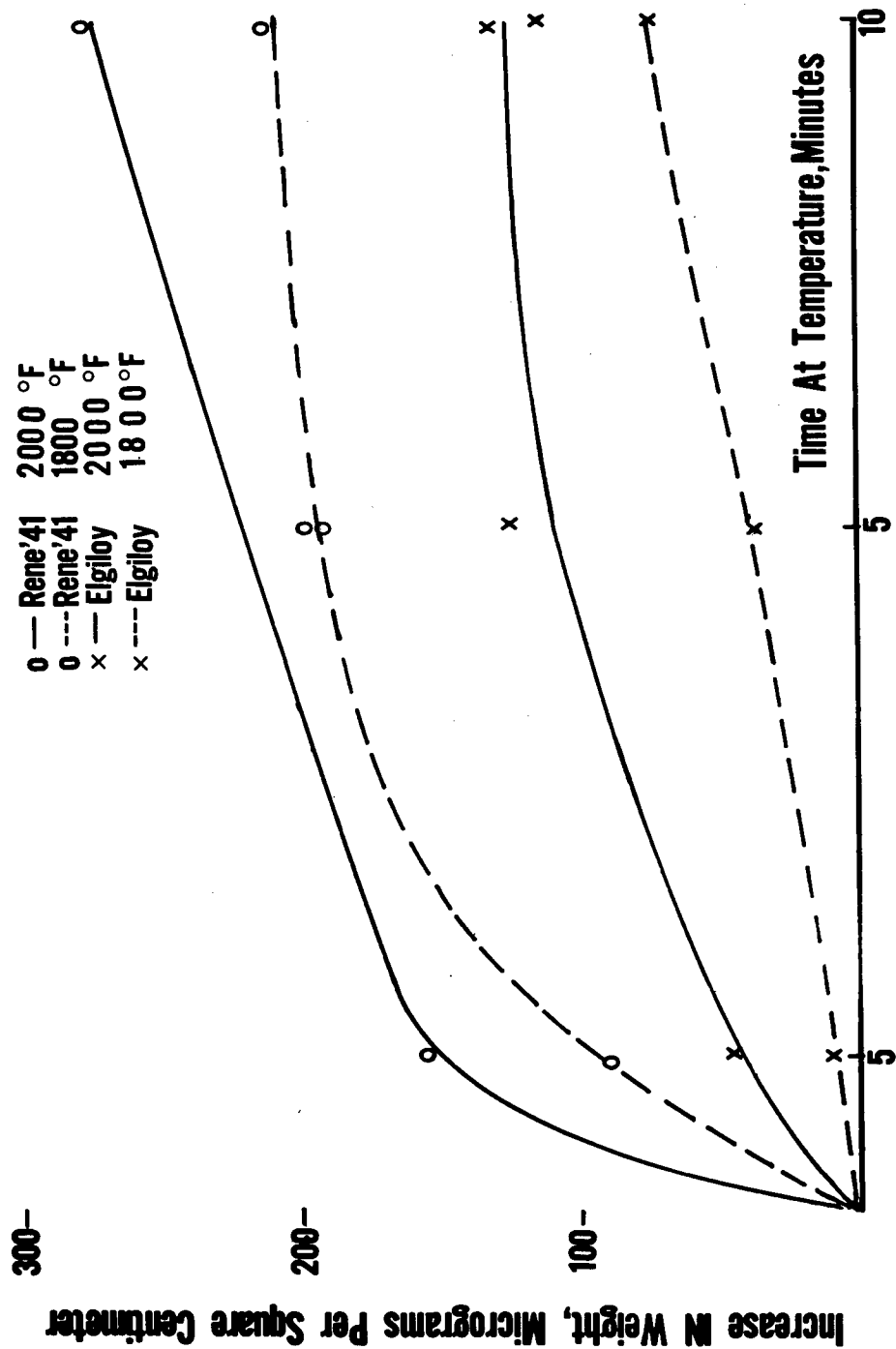


Figure 14.

COMPARISON of STRENGTH of TWO ALLOYS AFTER HEATING IN STAGNANT AIR 1 MIL FIBERS

TEMP. TO WHICH FIBERS WERE EXPOSED °F	HEATING TIME MINUTES					
	1		5		10	
	Elgiloy	Rene'41	Elgiloy	Rene'41	Elgiloy	Rene'41
ULTIMATE TENSILE STRENGTH p.s.i. × 10						
NOT HEATED	200	169	200	169	200	169
1500	194	203	179	207	169	200
1800	155	146	118	114	85	66
2000	113	130	87	Too Brittle	77	Too Brittle
ELONGATION %						
NOT HEATED	28	23	28	23	28	23
1500	21	13	13	13	7	8
1800	6	6	3	1	< 2	1
2000	6	3	5	0	3	0

Figure 15.

FIBERS of THE PRESENT and FUTURE

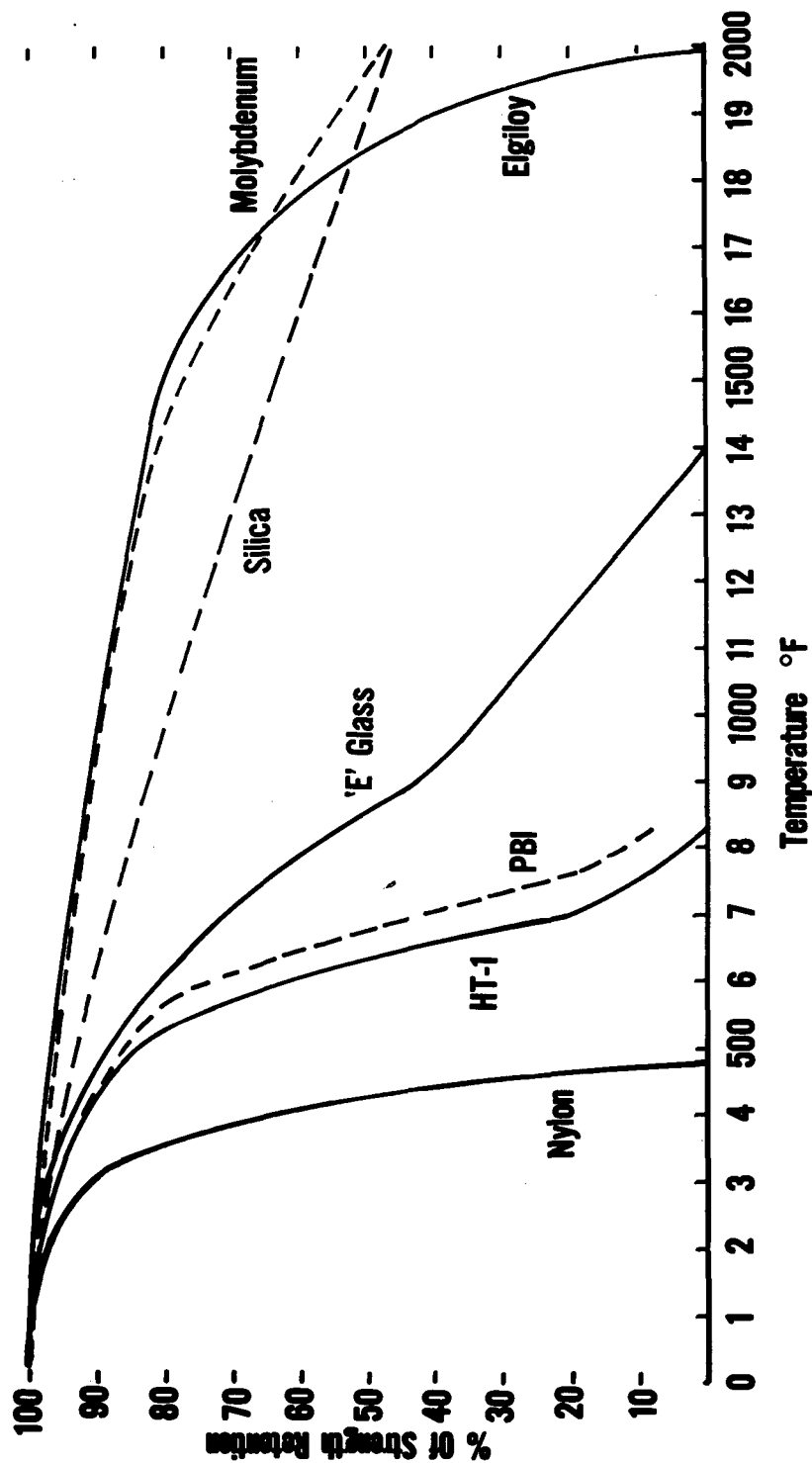


Figure 16.

ONE-WAY STRETCH MATERIAL WITH RESTRAINING CORD

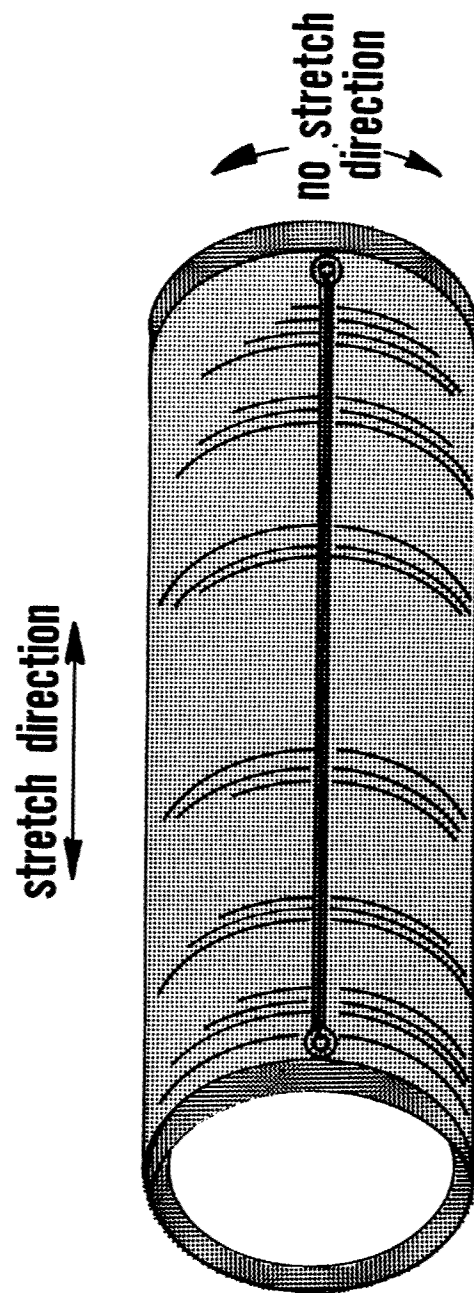


Figure 17.

NET TYPE STRUCTURE USED IN PRESSURIZED JOINT

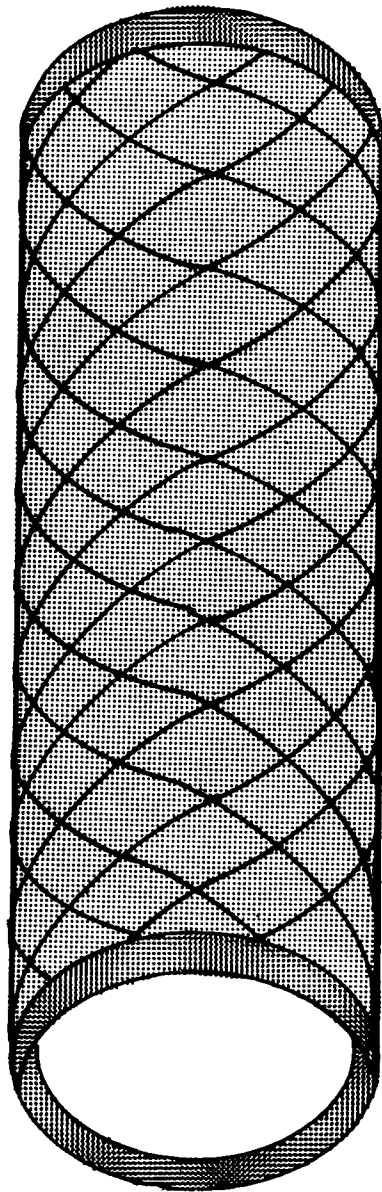


Figure 18.

NON-DESTRUCTIVE TESTING

Chairman

Mr. R. R. Rowand

Speaker

Mr. W. L. Shelton

Mr. E. M. McKelvey

Panel Members

Mr. G. W. King

Mr. E. Dugger

APPLIED RESEARCH PROGRAM FOR NONDESTRUCTIVE METHODS DEVELOPMENT

Richard R. Rowand

Directorate of Materials and Processes, ASD

Paralleling the omnidirectional advances in materials technology is progress in non-destructive methods development. As a category of test procedures, nondestructive techniques have been used successfully for centuries. Originally such tests were developed for gross detection capabilities, that is, separation of the good and bad. Gradually, through various improvements, these techniques were developed to measure a degree of acceptability. This trend has continued producing techniques of greater precision and accuracy in terms of meaningful information. Recent progress has added the potential of property measurements, and capabilities to measure material behavior and response to environmental variations. Therefore, nondestructive methods provide a scientific contribution to materials research, and assurance of reliability and integrity. The most outstanding single attribute of a nondestructive test is that it is economically advantageous.

In the development of methods for measuring the qualities or properties of materials in a non-injurious fashion, the Directorate of Materials and Processes directs an integrated program for providing nondestructive techniques for the Air Force.

From the study of material behavior or properties, this undertaking extends from that of exploring the unknown, to the development of new or improved techniques and their direct application to material problem areas. This concept or approach is ideal, and provides the necessary basis for future research and application programs.

Much of the nondestructive methods development has been after-the-fact in nature, by devising techniques to cope with specific problems as they arise. This will continue to be one of the more important contributions of the techniques. Of equivalent importance, is the general improvement of procedures and the creation of those with new or unique capabilities. Beyond this lies the lightly investigated region of using several forms of energy in a nondestructive manner to study various properties of materials and their behavior under a variety of environmental conditions. Through this type of research has come nondestructive techniques for measuring grain size, and the ability to measure or observe phase transformation and similar phenomena nondestructively.

To present a clear picture of these concepts in terms of the basic purpose, direction and progress, several programs will be related with future technical requirements cited.

For the past two years there has been an active program for the ultrasonic determination of actual flaw size in materials. While anomalies in materials have been detectable ultrasonically for over a decade, their exact physical location, size and other characteristics have been defined by comparison to various types of calibrated standards. These qualitative comparisons are normally adequate but certainly subject to considerable criticism. The standard blocks usually have flat bottomed holes, with the holes normal to the path of the sound waves. During actual material evaluations, the flaw is seldom normal to the sound beam, but at an angle and the amplitude of the signal is decreased. A curved flaw surface will give a smaller signal than an equivalent flat bottomed hole normal to the sound path. The result is obvious since smaller signals are readily interpreted as smaller discontinuities and could result in the use of unsatisfactory materials.

Improvement in past ultrasonic developments have logically and correctly followed electronic advances. The required information has largely been associated with appropriate electronics in terms of transmitting, receiving and displaying a propagated sound wave. Important as this is, the most critical factor is a fundamental understanding of the sound beam. The acoustic properties are paramount in successful inspection, with all electronics serving only as a media for information display.

Currently, three basic methods of presentation are in use for displaying the ultrasonic information existing within materials. These are A, B, and C scans, which are shown in figure 1. A-scan is a single line display in which time is measured on the horizontal axis and the amplitude of the echo from internal flaws on other material surfaces is measured on the vertical axis. By measuring the position of the echo on the time scale the depth of a discontinuity below the surface may be determined. The B-scan presentation gives a cross sectional view and displays the depth and extent on the horizontal axis as shown in figure 2. Physical position of the transducer is represented by the horizontal axis and is translated to an electrical signal by a data potentiometer. The C-scan, is the presentation which shows a plan view of flaw or flaws within a part and is analogous to a radiograph, as illustrated in figure 3. The result is a picture of the scanned surface area and location of flaws within this area without regard to depth. This is accomplished using two data potentiometers to record transducer position. Each of these presentations has advantages and in each there is a limitation in the ability to show volume and to give a complete picture. If we combine B and C scans, thereby deriving information in both the vertical and horizontal planes, we will be able to more fully describe the contents of a given material.

This was done using a single transducer with an electronic combination of the B and C-scan systems. Basically the system consisted of the transducer scanning horizontal back and forth across the part, with the transducer being stepped over mechanically after each length of travel. This displacement is electrically synchronized through the use of data potentiometers to the displacement on the oscilloscope screen. Summation of all cross sectional scans on an oscilloscope results in an isometric projection of a section of a material and its internal inhomogeneities. Figure 4 illustrates the principle. The problem is still not solved. The single transducer views in only one direction and while depth, location and extent are shown, this is in part the result of data potentiometer translation. Information with respect to discontinuity volume is still not available. Therefore, while a single transducer can be effectively employed to produce isometric views it is still limited in a practical realistic sense because a single transducer can only receive responses from surfaces relatively normal to the path of the sound beam defining only one or part of one dimension of the flaw.

The solution to this problem is viewing a material from more than one direction. The first approach was through the use of a multiple transducer system. A complex of three or more matched transducers were used. A schematic of the system is shown in figure 5. Part A shows the information from the normal transducer, No. 1. Part B shows the data derived by transducer No. 2. Part C is the information from the third transducer, and Part D is the composite scans of all three transducers. Combining this with the previously discussed scanning will produce an isometric view of depth, location, and the important property, volume. Figure 6 illustrates the equipment in laboratory form.

Since the velocity of sound is known or easily determined for most materials, the transducers may be angled to give a wide coverage of the media and its discontinuities wherever necessary. Selection of the appropriate angle is made through the use of Snell's Law where

$$\frac{\sin i}{\sin r} = \frac{V_1}{V_2}$$

where i = angle of incidence
 r = angle of refraction
 V_1 = Velocity - medium 1
 V_2 = Velocity - medium 2

This is necessary since the angle of propagation in most materials is appreciably different from the angle or direction of sound propagation from the transducers. The most difficult requirement of this approach is the presentation of the composite scan and the view seen by each transducer at the proper time and location on the oscilloscope screen. This, is merely an electronics problem and not overly difficult.

The success of the program is best described pictorially comparing the single and multiple transducer systems. Figure 7 shows a 5/64-inch flat bottomed hole drilled to a 3/4-inch depth in an aluminum alloy block. Using the single transducer system at 10 and 25 megacycles the hole is clearly defined as well as both front and back surfaces. In striking comparison the multiple transducer system shows additional information, V12 the sides of the hole. In figure 8, the true contribution of the system is seen. Representing a crack open to the surface is a circular saw cut 5/8-inch deep. The single transducer sees only the peak, whereas the multiple transducer system relates depth and contour of the cut. With the single transducer, the shadow of the flaw is seen on the back surface, indicative that the sound energy was reflected but not in a direction that would be detectable by the transducer.

The study proved the feasibility of the concept. Research is continuing on a second approach yielding greater detail and overcoming some of the limitations of the basic system. All of the limitations are directly related to the transducers. The multiple transducer system is complex, slow, and limited in ability to scan unusual surface configurations.

In considering the limitations of the system it must be remembered that the interpretation of discontinuity sizes is not limited by acoustic parameters but by the nature of the discontinuity that may prevent complete ultrasonic energy reflection to the transducer. Therefore, the transducer and acoustic characteristics are the factors of greatest importance. As a consequence, the entire system has been re-evaluated and re-designed from the sound beam requirements. The disadvantage of further exploitation of a multiple transducer system is the electronic complexity which would result in integrating many transducers. As the system complexity increases, the ability to scan rapidly, and also to scan contours, becomes a serious problem. A single search transducer, one manipulator and one electronic channel would be the optimum choice and this approach is currently being pursued. Figure 9 shows the new search sweep manipulator system with the transducer, data potentiometers, and the various drive mechanisms identified. This unit is designed to oscillate the transducer in a sinusoidal motion over a calculated pre-set path. This is necessary to produce a constant speed of the acoustic beam at various angles of refraction in the metal as the surface is scanned. The manipulator system is capable of positioning the transducer in such a way as to hold the point of incidence at which the sound beams enter the metal at an individual point. The unit is capable of varying the

speed of the sweep and the angle through which the transducer is swept. The sweep speed is variable from 0 to 110 sweeps per minute and the angle of sweep can be varied from 0 degrees to ± 18 degrees. The angular motion of the transducer is more than enough to exceed the critical angle for most materials. Another very important advantage of the system is that the transducer may be operated at distances from the metal surface ranging from 1/4 inch to 4 inches.

The sweep circuits have been designed coincident to the path of the ultrasonic energy. If the ultrasonic beam makes a ± 90 -degree sweep from the normal plane within the part, then the electronic beam in the presentation must show the same path. The major change has been the substitution of the multiple transducer system for one using a single transducer with a compound sweep system duplicating the actual sound beam pattern or acoustic path.

Complete development of this system will provide the capability of presenting inhomogeneities in their true perspective in relation to boundary interfaces and will establish accurate and critical material evaluations.

In contrast to the normal research and development programs for nondestructive methods, the Directorate of Materials and Processes has a series of objective projects dealing with nondestructive studies of properties and behavior of materials. These projects are profound in nature and represent tools heretofore unavailable for studying materials properties, structure and behavior.

The principles are clearly shown in a program where the metallurgical changes in metals subjected to stress cycling, are studied with ultrasonic propagation techniques involving measurement of attenuation and velocity. The data supports the theory that cycling results in a dying-out of dislocation damping effects, as well as recovery in early stages of cycling. Continued cycling, results in additional changes that are related to slip processes through the development of defects and strain regions. With these measurements, the surface of the metal samples are further studied by optical and electron microscope techniques. Examples of the changes during a material's life are shown in the following figures: Figure 10 represents a series of maximum and minimum recorded values attained during each cycle over 10^4 cycles. The material is 1100 aluminum alloy and stressed equally in tension and compression. Figure 11 shows the observation of recovery. The average values of attenuation are shown as a function of cycles, with the discontinuities representing recovery during interruption of the cycle. This material is 1100F aluminum alloy at 9000 psi and was cycled in both tension and compression.

Further research is being pursued to measure ultrasonic attenuation changes in both single and polycrystalline metals under cyclic straining and to study the correlation of these indications with the metallurgical and other mechanisms involved. Success in this endeavor will provide valuable contributions to materials technology as a means of studying both material behavior and properties.

This research has another closely related investigation which is directed toward a specific problem, that of residual stress measurement. A fact often overlooked when mentioning residual stress is, that such a system of stresses may be beneficial rather than detrimental. These stresses, that exist in a body free from external forces, have been shown to increase fatigue life when they exist as compressive surface stresses. The increasing interest in residual stresses and their importance has emphasized the need for measurement techniques, by nondestructive methods. Almost all techniques

available are destructive with the exception of X-ray, which is nondestructive. However, there are many disadvantages and difficulties associated with its use, plus the fact that only surface stress can be measured.

After a very extensive literature and theoretical analysis of the feasible methods, the study of ultrasonic propagation in metals indicated the most promise.

What happens to a propagated sound beam in a material subjected to stress? Are these changes solely the result of stress? These two questions have in part been answered through extensive studies. Figure 12 shows the $(\frac{\Delta v}{v})_s$ versus stress in aluminum. This relationship of velocity and stress is not new and unique, however past efforts have not been directed toward use of this phenomena. Primary attention has been given shear wave bi-refrignence or polarization under uniaxial stress. Shear wave bi-refrignence was recognized early in the program as an excellent indication of stress. The magnitude of stress-induced bi-refrignence varies linearly with stress level. There are still many barriers to overcome since anisotropic factors influence the results and must be known, or be small in comparison to the stress effects; nevertheless a step forward has been made.

There are several new techniques being applied in nondestructive materials analysis. One of these being explored is electrical resistivity. While electrical resistivity measurements have been common as a metallurgical tool, the particular concept which will be discussed is quite unique in approach. The basic theory involves the measurement of voltage decay produced by a created degeneration of magnetic flux within a specimen whose permeability is approximately equal to one. Present experiments utilize a non-contact eddy current principle for which equipment and accuracies are being confirmed. The transducer consists of a driver and a pick-up coil wound concentrically on a coil form in which the material to be evaluated is inserted. The outer, driver coil, is energized, and at cut off, the decay in the magnetic flux is observed by the pick-up coil as a voltage decay which is measurable. The rate of this degeneration or change of slope is measured. From these measurements resistivity can be calculated, since the decay is an exponential function in the latter portion of the degeneration. The advantages of the technique are that no direct contact is necessary and specimen shape is not important for relative measurements, that is, assuming only the changes in resistivity values in a material are desired. Absolute measurements necessitate that specimen dimensions be known. Relative measurements with an accuracy of about 2 percent are anticipated. The method offers advantages as a corollary to dynamic modulus measurements and other techniques valuable to mechanical metallurgy. Initial studies have been limited to the evaluation of the method as a measure of room temperature precipitation in 2024 aluminum alloy from the solution heat treated condition to that of T-4 or room temperature aged condition.

Another relatively recent technique involves the use of infrared. Such a method may be considered fundamentally as an extremely sensitive method of measuring heat transfer in materials. As a consequence all inhomogeneities affecting thermal transmission should be detectable. Research has been initiated for a basic workable system for defining detectability, resolution and the parameters affecting reliable use of infrared techniques. Early studies will be concentrated on gross defects. It is anticipated that eventually the system will have capabilities of measuring various metallurgical and other properties at room and elevated temperatures. One of the fortunate aspects of this undertaking is the recent wealth of background information in military, astronautical and industrial applications. Many of the limitations have been defined and are not technological

barriers but merely require research skill to advance the state of the art in the direction of material analysis. The scheme of the procedure used employs the concept of scan heating and detecting transient effects. Deviating now to ceramic materials, we find that there are ample areas of concern for which nondestructive methods have not been adequate. Ceramic coatings on metal substrates, for example, is an extremely difficult problem area. Here we are dealing with a specific problem — integrity. Integrity is two-fold in a sense, considering both the coating itself and its bond to the substrate. The media involved are of inherent complexity. The worst enemy of problem solution is the multitude of factors associated with integrity which range from voids, to lack of bond, to such concealed variables as oxidation resistance. The object of defining these characteristics nondestructively has been pursued, by using ultrasonic energy, and by emphasizing continuity measurements of the ceramic-metal bond as the first issue to be settled. Three approaches have been investigated, namely: charge scanning, surface wave, and intermodulation techniques. Early studies involved understanding of these little known ultrasonic phenomena, and as experience is gained in their application to integrity problems, their resolution and sensitivity is being found to be quite remarkable.

Another aspect of ceramic and related materials which is receiving considerable attention is the analysis of brittle fracture behavior nondestructively. Through diffraction studies, radioactive tracers, capacitance, resistance and other techniques, surface and internal factors related to behavior are under scrutiny. The effects of orientation, anisotropy and other parameters are being investigated. Surface phenomena are stressed because of their importance and the desire to develop techniques capable of locating sites of crack formation prior to initiation.

In summarizing the requirements in the field of nondestructive methods development, we find that continuation and advancement of techniques through research will provide improved and new processes for a wide variety of purposes necessary to the basic understanding of materials, their behavior, and their use in providing optimum materials for precision Air Force systems.

BIBLIOGRAPHY

1. G.J. Posakony and M.R. Loetz "Investigation of Methods for Determining Actual Flaw Size in Materials by Nondestructive Ultrasonic Techniques", WADC TR 59-302, 1959.
2. R.R. Rowand, E. Dugger and G.J. Posakony, "Three-Dimensional Presentation of Flaws", Paper given at the 20th Annual Meeting of the Society for Nondestructive Testing, October 1960.
3. L.J. Anderson and G.J. Posakony, "Investigation of Methods for Determining Actual Flaw Size in Materials by Nondestructive Ultrasonic Techniques", Progress Reports 1, 2, 3 and 4. Contract AF 33(616)-7279 1960-61.
4. E. Dugger and G.J. Posakony, "Determination of Actual Flaw Size in Materials by Ultrasonic Techniques", Third International Conference on Nondestructive Testing, March 1960.
5. Rohn Truell and Akira Hikata, "Fatigue and Ultrasonic Attenuation", Special Technical Publication # 215, American Society for Testing Materials (1957).
6. R.F. Hanstock, "Fatigue Phenomenon in High Strength Aluminum Alloys", Journal Institute of Metals 83, 11 (1954).
7. Rohn Truell, Bruce Chick, Amos Picker and George Anderson, "The Use of Ultrasonic Methods to Determine Fatigue Effects in Metals", WADC Technical Report 59-389 (1959).
8. A. Hikata, R. Truell, B. Chick and K. Lücke, "Sensitivity of Ultrasonic Attenuation and Velocity Changes to Plastic Deformation", Journal of Applied Physics 27, 396 (1956).
9. A. Granato and K. Lücke, "Theory of Mechanical Damping Due to Dislocations", Journal of Applied Physics 27, 583 (1956).
10. M.S. Hunter and W.G. Fricke, Jr., "Effect of Alloy Content on the Metallographic Changes Accompanying Fatigue", Proceedings American Society for Testing Materials 55, 942-953 (1955).
11. M.S. Hunter and W.G. Fricke, Jr., "Metallographic Aspects of Fatigue Behavior of Aluminum", Proceedings American Society for Testing Materials 54, (1954).
12. Rohn Truell, et. al., "Ultrasonic Methods for the Study of Stress Cycling Effects in Metals", WADD TR 60-920, (1960).
13. Fred R. Rollins, "Study of Methods for Nondestructive Measurement of Residual Stress", WADC TR 59-561, (1959).
14. Fred R. Rollins, "Ultrasonic Methods for Nondestructive Measurement of Residual Stress", WADD TR 61-42, Part I, (1961).

BIBLIOGRAPHY (Cont'd)

15. C.P. Bean, R.W. DeBlois and L.B. Nesbit, "An Eddy-Current Method for Measuring the Resistivity of Metals", G.E. Report No. 59-RL-2282M, October 1959.
16. R.C. Griffis, "Application of the Eddy-Current Method for Measuring the Resistivity of Metals", G.E. Report No. 60-LMC-151, April 1960.
17. H.L. Hackforth, "Infrared Radiation", McGraw-Hill, 1960.
18. Dale R. Maley and Jack T. Collins, "Applied Research to Establish Infrared Detection Methods for Nondestructive Analysis of Materials", Progress Report No. 1 under Contract AF 33(616)-7725, April 1961.
19. R.R. Whymark, and W.E. Lawrie, "Ultrasonics and Ceramic Coatings", WADD TR 60-157, May 1960.
20. W.E. Lawrie, "Ultrasonic Methods for Nondestructive Evaluation of Ceramics Coatings", WADD TR 61-91, Part I, March 1961.
21. Julian H. Lauchner, Dwight G. Bennett and George L. Morgan, "Nondestructive Tests for Ceramic, Cermet and Graphite Materials", WADC TR 59-412, November 1959.
22. J.L. Pentecost and J.H. Lauchner, "Nondestructive Analysis of the Brittle Fracture Behavior of Ceramic Materials", Progress Reports 1 and 2 under Contract AF 33(616)-7347, December 1960 and February 1961.
23. L.J. Mattek and R.D. Woodward, "Correlation of Tensile Properties of Steel Castings and Material Imperfections as Determined by Radiography", WADD TR 60-450, November 1960.
24. R.E. Kleint, R.D. McKnown and J.B. Ramsey, "Application of Ultrasonics to Solid Rocket Systems", WADD TR 60-553, October 1960.
25. R.B. McCauley and Quentin Van Winkle, "Research to Develop Methods for Measuring the Properties of Penetrant Flow Inspection Materials", WADD TR 60-520, Part I, June 1960.
26. R.C. McMaster, A.T. D'Annessa and H.W. Babel, "Evaluation of Brazed Honeycomb Structures", WADD TR 60-393, September 1960.
27. G.L. Cross, R.E. Kleint, R.D. McKnown, "Research and Development Leading to the Establishment of Ultrasonic Test Standards for Aircraft Materials", February 1960.

"A" SCAN PRESENTATION

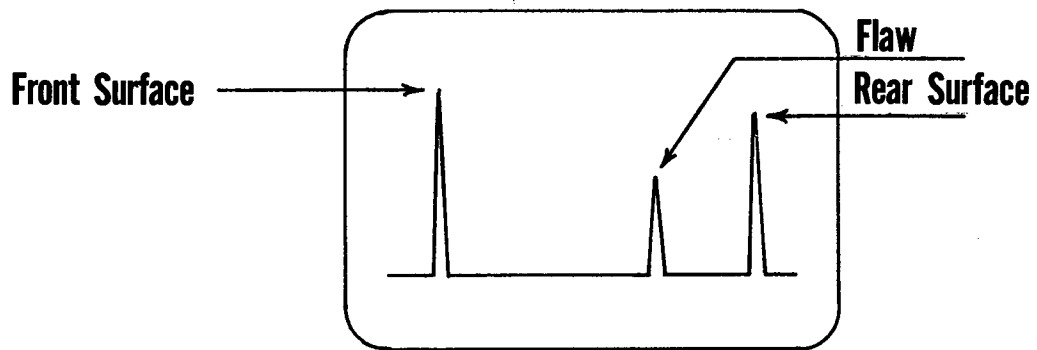


Figure 1.

"B" SCAN PRESENTATION

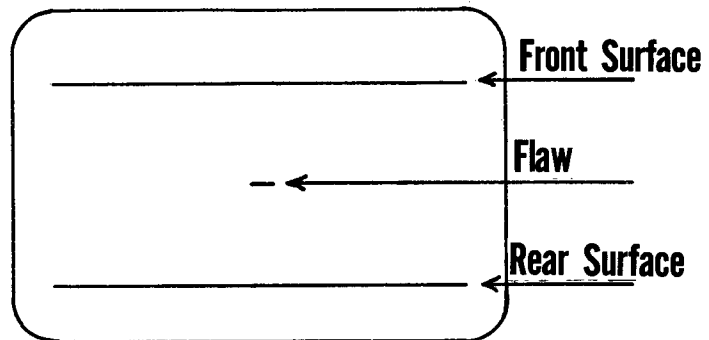


Figure 2.

"C" SCAN PRESENTATION

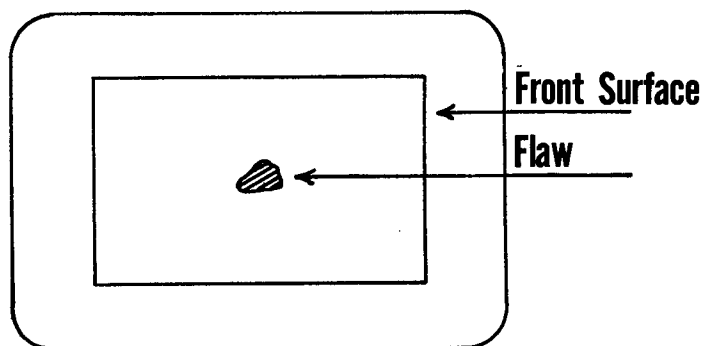
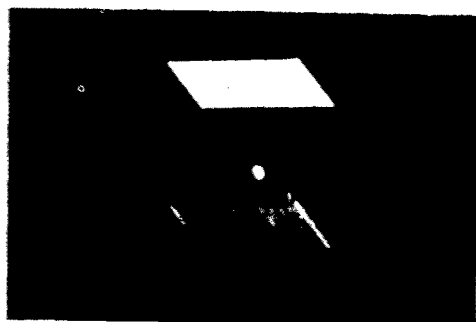
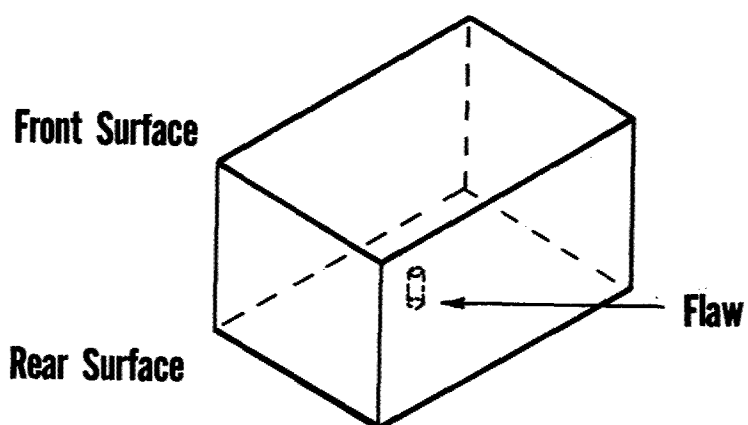
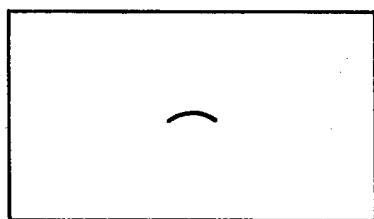
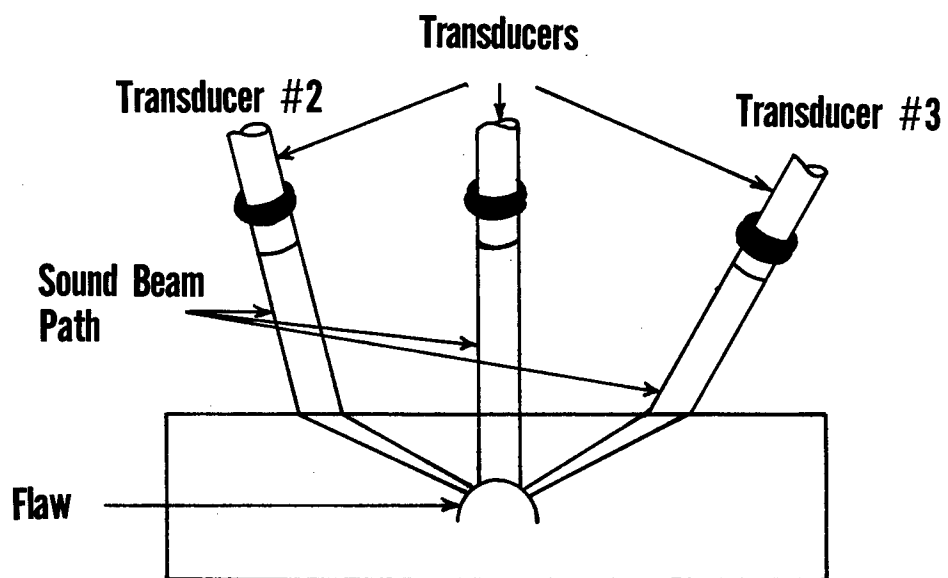


Figure 3.

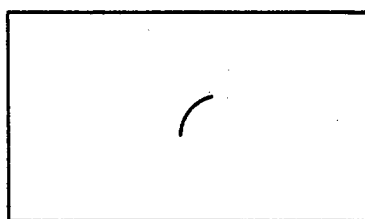
STANDARD FLAT BOTTOMED HOLE



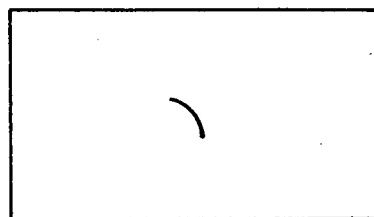
MULTIPLE TRANSDUCER PRESENTATION



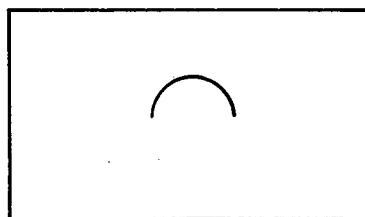
A



B



C



D

Figure 5.

PHOTOGRAPH OF LABORATORY EQUIPMENT

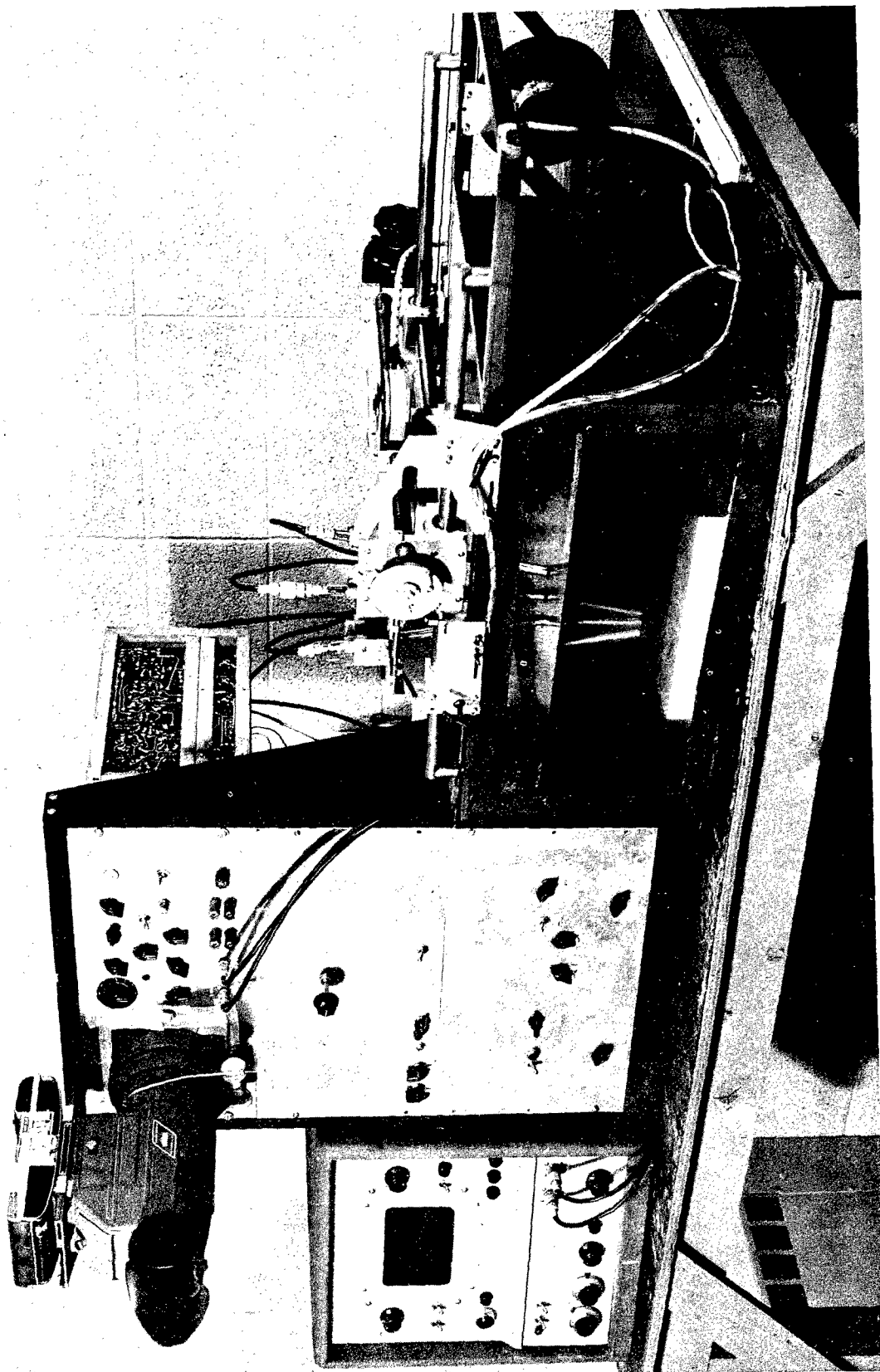
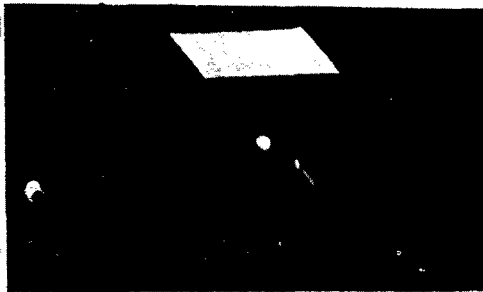
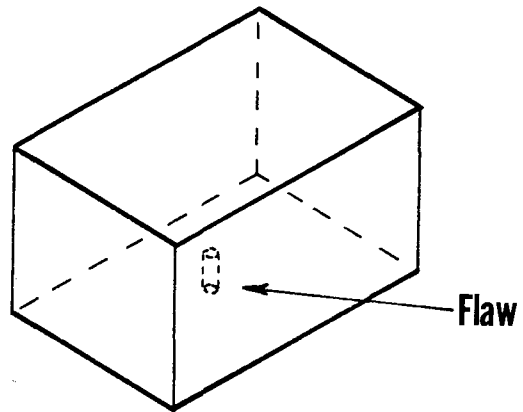


Figure 6.

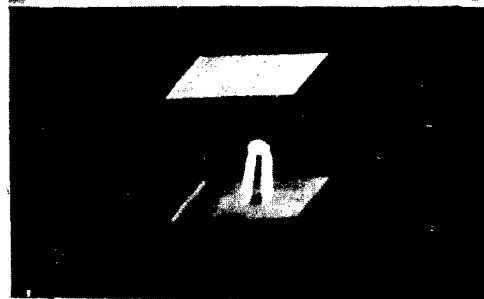
STANDARD FLAT BOTTOMED HOLE

Front Surface

Rear Surface



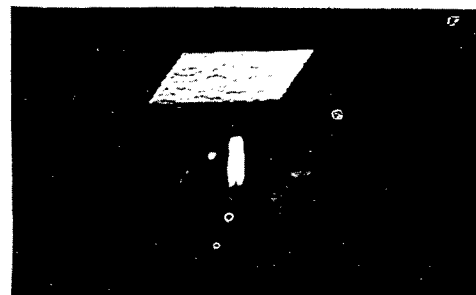
Single Transducer 10.0 Megacycles



Multiple Transducers 10.0 Megacycles



Single Transducer 25.0 Megacycles



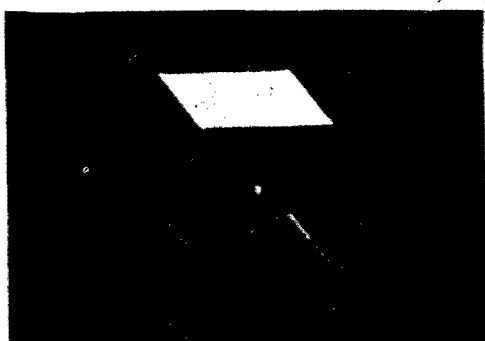
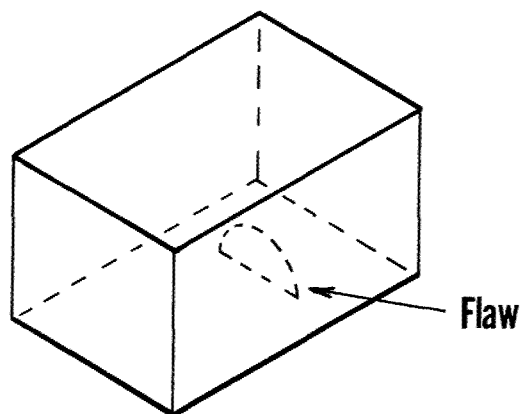
Multiple Transducers 25.0 Megacycles

Figure 7.

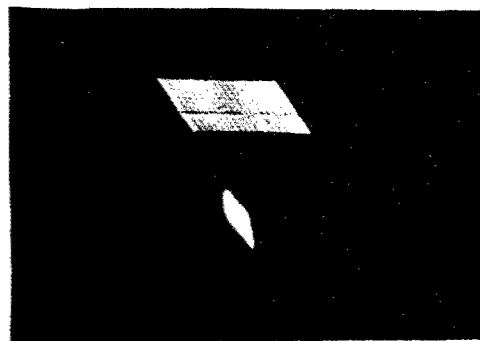
SAW CUT

Front Surface

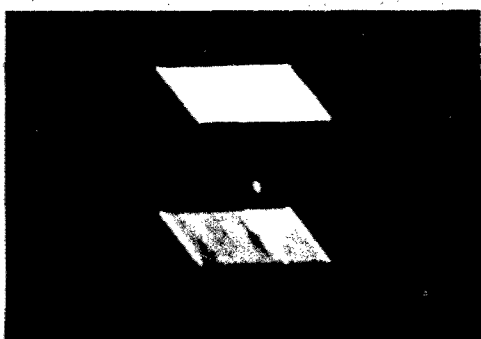
Rear Surface



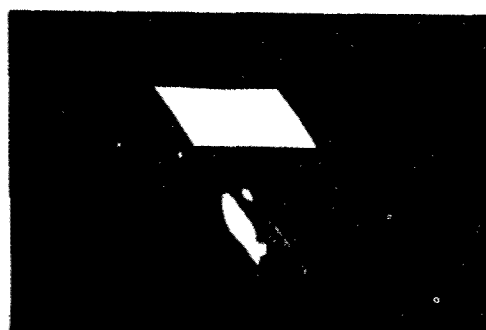
Single Transducer 10.0 Megacycles



Multiple Transducers 10.0 Megacycles



Single Transducer 25.0 Megacycles



Multiple Transducers 25.0 Megacycles

Figure 8.

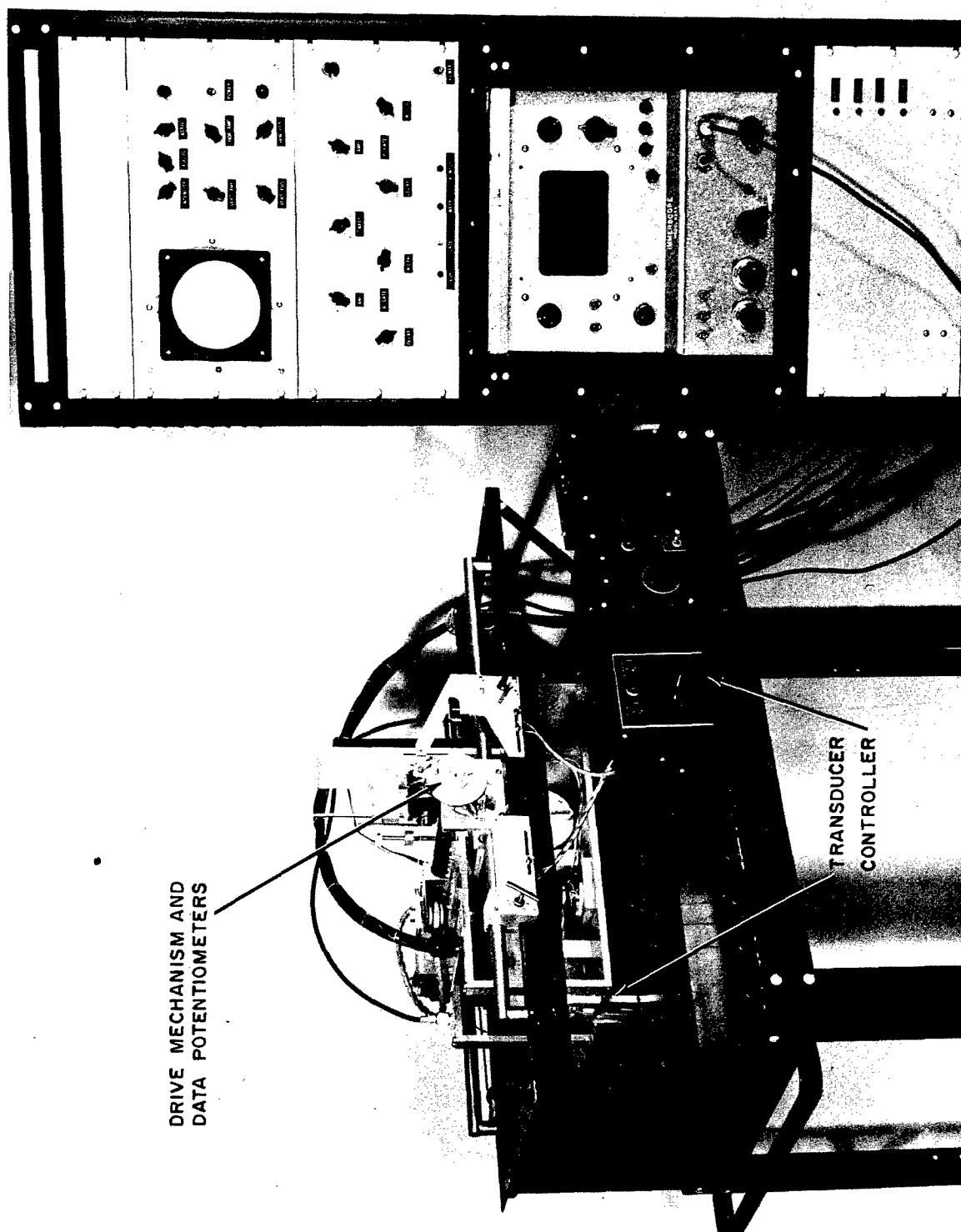


Figure 9.

MAXIMUM & MINIMUM VALUES OF ATTENUATION ATTAINED DURING CYCLE AS A FUNCTION OF THE NUMBER OF CYCLES

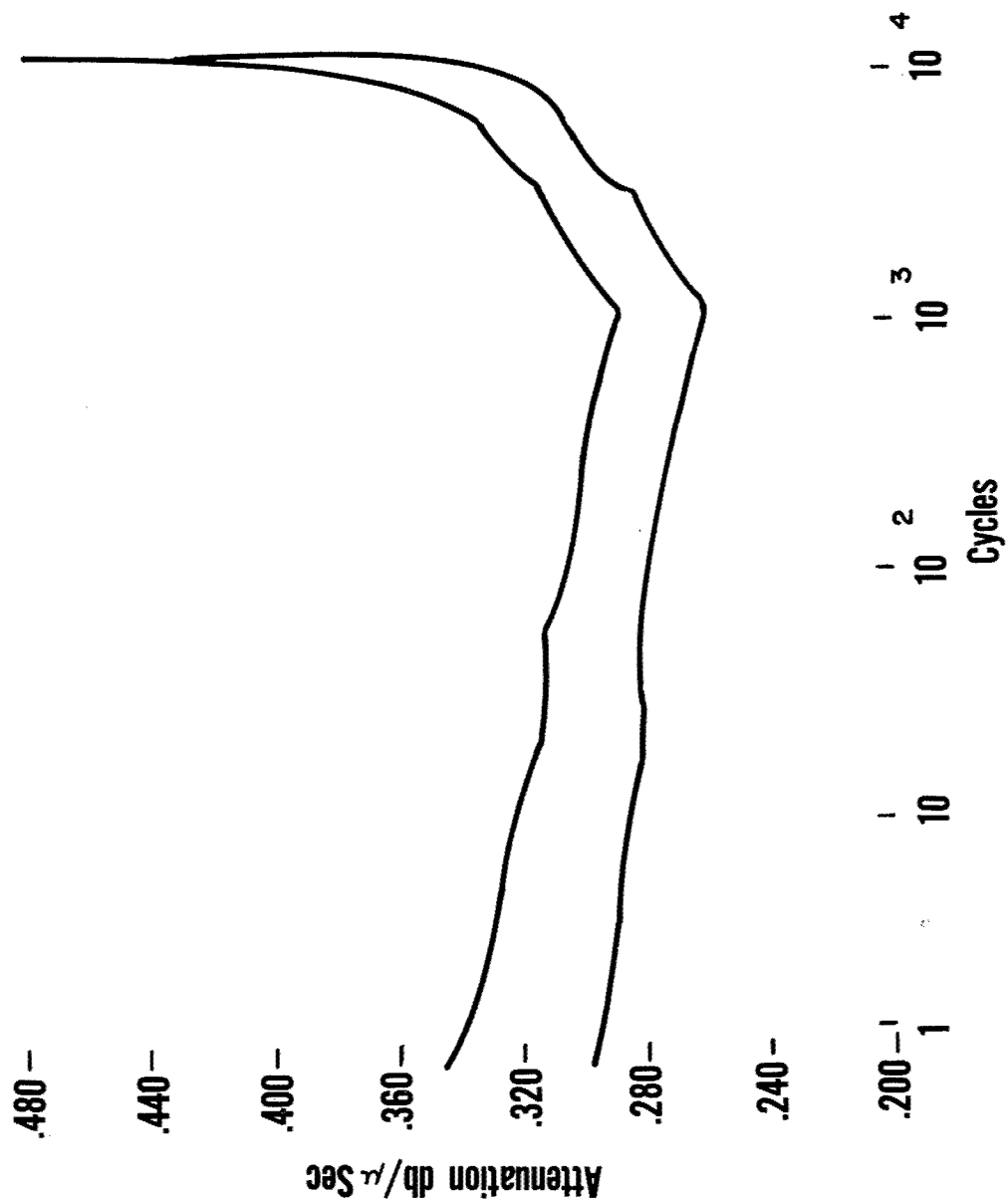


Figure 10.

RECOVERY OF ATTENUATION

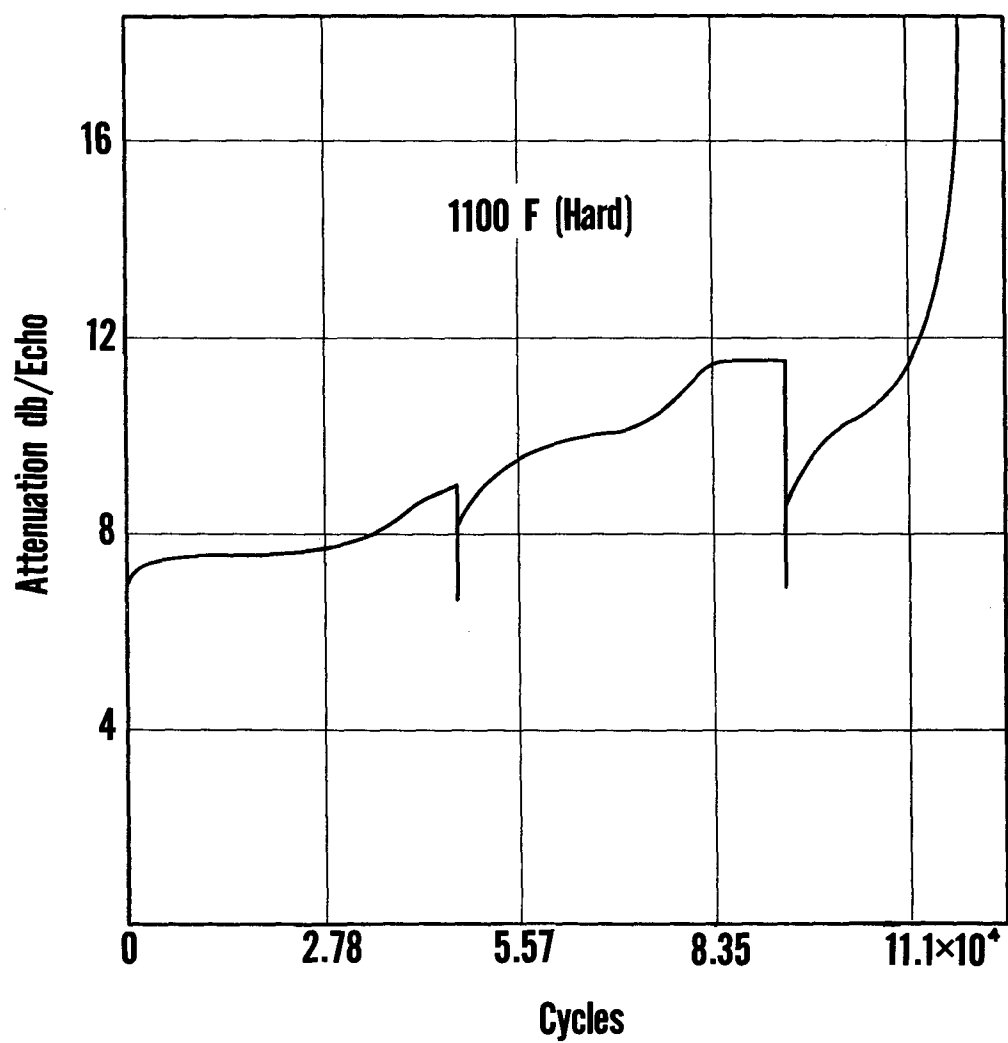


Figure 11.

$\left(\frac{\Delta V}{V}\right)$ VERSUS STRESS IN ALUMINUM AT TWO FREQUENCIES

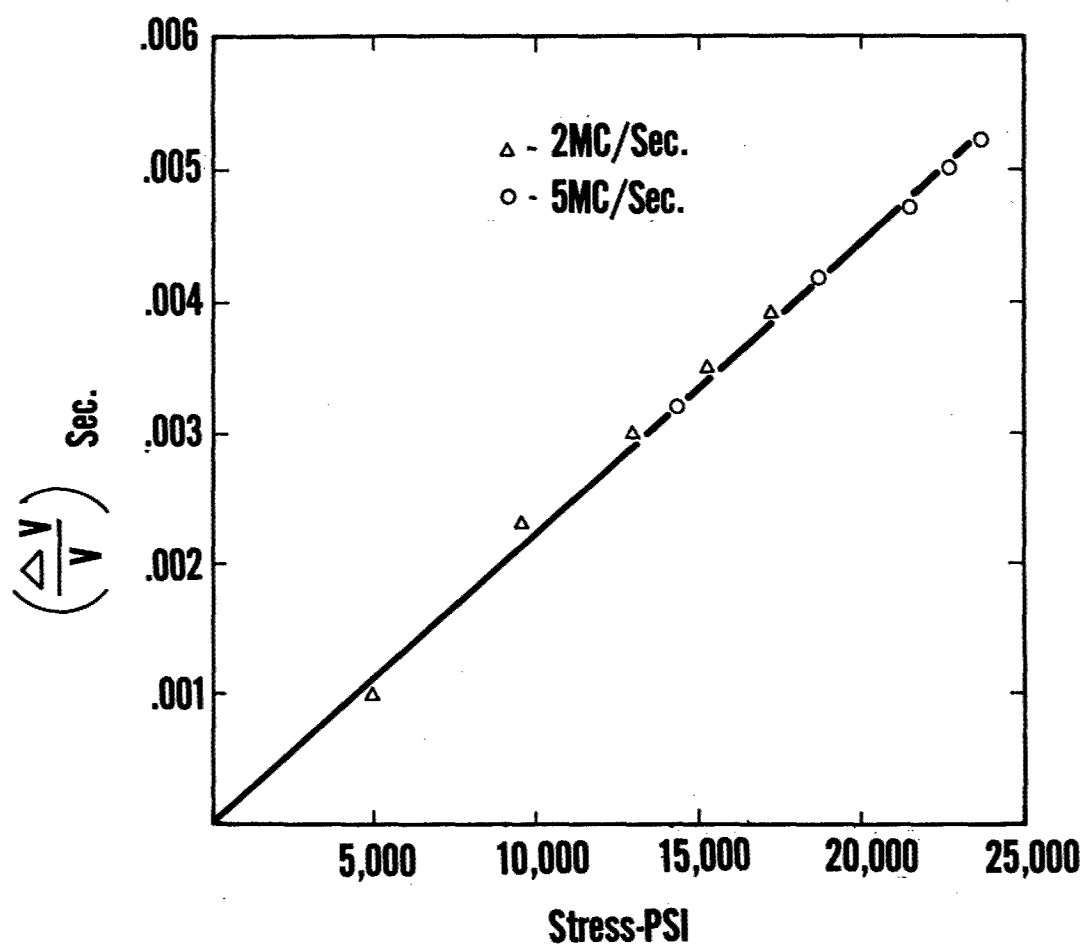


Figure 12.

THE NONDESTRUCTIVE MEASUREMENTS OF SURFACE CONNECTED DISCONTINUITIES

William L. Shelton

Directorate of Materials and Processes, ASD

Introduction

To obtain the high performance in modern aircraft and missiles, it is necessary to test many of the components by high unit stresses, and to eliminate redundant structures, because failure of any one component could lead to catastrophic results. To secure positive reliability and to satisfy the high performance requirements, testing often must subject individual components to high unit stresses. It is well known that failures in highly stressed areas are often caused by the presence of cracks or other surface discontinuities which produce stress concentrations. For this reason, tests of raw materials must be continued until their quality is assured. Since destructive testing can give assurance only on a statistical basis, nondestructive testing is preferred where it can be used.

Nondestructive tests for surface flaws necessitate identical or nearly identical flaw indications for the same flaw regardless of the operator, equipment used, or the testing media. To achieve this, a uniform operating procedure, and standard equipment and testing media are required. Many investigators are attempting to do just that with nondestructive testing systems. A review of some of the work being done will aid in an understanding of the parameters related to the nondestructive test procedures, the "penetrant inspection processes."

Types of Penetrants

The penetrant inspection process involves treating parts by immersion in a penetrant fluid containing a visible or fluorescent dye. The penetrant entering the flaw becomes trapped and remains even after the surface is cleaned by solvent removal or emulsification and water washing. The part is then dried. The trapped penetrant will exude from the flaw, in most cases, with the aid of a developer that acts as a blotter and provides a contrasting background (see figure 1).

At the present time, we have water washable penetrants and post emulsifiable penetrants of both the visible and the fluorescent variety. The water washable type penetrant is less sensitive than the post emulsifiable penetrant because penetrants containing an emulsifying or solubilizing agent are more readily removed from small flaws.

Water washable penetrants are simply called one step process materials. Cleaned and degreased parts are immersed in the penetrant for a specified time, then washed with water to remove the surface penetrant. After washing, the part is dried and examined under the proper light to insure that all surface penetrant was removed. Developer is then applied, and, after the appropriate dwell time, flaw indications will appear (see figure 2).

Penetrants of the post emulsifiable type are called two step process materials; they require the use of an emulsifier to render the excess penetrant removable by washing with water. Cleaned and degreased parts are immersed in the penetrant for a specified dwell time, then drained thoroughly and immersed in an emulsifier for the required dwell time. The parts are then washed and flaw indications will appear (see figure 3).

Properties of Penetrant Materials

Liquid penetrants depend upon surface tension (capillary action) to move the liquids through narrow apertures. Use of liquid penetrants is limited to exploration of accessible surfaces and channels or apertures open to the exposed surfaces of the test object. This phenomena may be more clearly understood through an investigation of the mechanism by which liquids penetrate cracks.

One of the outstanding requirements of a penetrant is its wetting ability. A penetrant that has good wetting properties will spread smoothly and cover the entire surface. Penetrants that do not have good wetting ability, on the other hand, will pull back on themselves, thereby leaving areas of the test surface uncovered. The primary factors involved are surface tension and contact angle.

Direct surface tension measurements can be made by using a Du Nuoy Ring Tensiometer. Contact angle measurements can be made by using the method of Langmuir and Schaffer.

From a study of the factors affecting surface tension and contact angles of penetrants, we see that the driving force in the penetration process is the product of solid-liquid surface tension, $\gamma \frac{S}{L}$, and $\cos \theta$, where θ is the contact angle between the air-liquid and liquid-solid interfaces. The contact angle must be 0 degrees to promote spontaneous spreading of liquids on solid surfaces. For spontaneous spreading of liquids on metal, Zisman found that the liquid surface tension must be less than 22 dynes/cm.

The investigation up to this point reveals the direction of a spontaneous process, but it yields no information as to the rate of the process or the mechanism involved. Measurement of the rate of crack penetration must be investigated under a variety of conditions of temperature, liquid viscosity, surface tension, and contact angle measurements to provide additional information for establishing a mechanism for the penetration process.

Methods for making direct studies of penetration rates in the crack itself would be difficult to develop; however, there is a close relationship between rates of spreading on flat surfaces and penetration rates in the crack. An investigation of the work of Zisman reveals that the spreading of a liquid on a high energy surface such as metal results in (1) the formation of a single mono layer of liquid ahead of the bulk liquid and (2) the subsequent spreading of the bulk liquid on the surface of its own mono layer. This being true, a liquid is unable to spread on its own mono layer when the surface tension of the liquid is higher than the critical surface tension of the mono absorbed layer. Theoretically, the best penetrant would be one for which the rates of the formation of the mono layer would be high and the bulk viscosity low.

Crack Penetration

Another interesting aspect concerning the process or processes which will cause liquids to enter cracks is related principally to the immersional wetting system. This system is represented in figure 4. The degree to which penetration will extend in this system depends upon whether the air in the crack is trapped or has escaped.

Experience has shown that all or most of all of the air is displaced. Two conditions exist which contribute to the displacement of air. First, as penetration proceeds, the air in the crack is placed under a higher pressure than under initial conditions. This causes higher solubility in the penetrating liquid thus bringing out the eventual transfer of the air

to the external gas phase. Second, assuming that each crack is not of uniform width and that one section of the crack will be penetrated before the other, air is then discharged at one section while penetration occurs at another.

For extreme conditions where air is trapped in the crack, the penetration of the crack by the liquid will increase the pressure of the trapped air from P_1 to P_2 as the liquid moves from position d_1 to d_2 (see figure 4). Using the relationship of surface tension and contact angle for typical penetrants, one finds that the crack width which will fill up 50 percent is about 0.6 microns, with wider cracks filling to a lesser extent.

Experience has shown that liquids achieve good penetration of cracks which are much larger than 0.6 micron. We may conclude then that air is displaced from the crack as the liquid enters.

Variations in crack width can also lead to expulsion of air from the crack (see figure 5). Performing applicable equations for theoretical wetting and balance of forces will show that the liquid flows in at "A" and that air is released at "B," eventually filling the crack. In both cases (figures 4 and 5) the equations indicate that the condition of high surface tension and low contact angle favor maximum penetration.

Intensities of Flaw Indications

Investigations of the intensity of flaw or defect indications as a function of detection sensitivity has been mainly concerned with the fluorescence of penetrants. Fluorescent brightness of a liquid penetrant is a key property in determining the penetrant's overall performance as an aid in the detection of cracks or surface flaws in solid objects. Various methods are being used to measure the fluorescent brightness of penetrants.

One method currently used compares the detection intensity of two strips of filter paper, one carrying a reference penetrant or fluorescence standard, the other a penetrant which is being rated. Both penetrants are diluted in a volatile solvent; filter paper test specimens are dipped into this solution, dried, and measured for fluorescent intensity by reflection. In general, this test procedure gives variable results because dye concentration of penetrants tested are not known; thereby, the type of solvent used can enhance fluorescence in some penetrants but reduce it in others. Figure 6 shows the results of dilution of a penetrant using several solvent systems.

A second method developed through the investigation of the Albein Reid Foundation measures fluorescence sensitivity rather than fluorescence brightness. This method is called the "meniscus method," which makes use of an optical, flat glass platten and a convex lens ground to a spherical surface having a radius of curvature of 106 cm. A black light source and a camera are used to photograph the fluorescence pattern of the liquid penetrant placed between the lens and the optical flat. This is arranged by placing a drop of penetrant on the flat platten and the lens on the drop to form a meniscus shaped film of liquid, whose thickness increases from zero at the point of contact to an appreciable value some distance from the center. It is known that fluorescence intensity increases continuously with the thickness of a liquid film. Since this is true, we may expect that a non-fluorescent "black" spot will appear whose measure will provide an index to determine ultimate dimensional sensitivity of a particular penetrant. One advantage of this method is that photographic records can show a dark spot in addition to a uniform brightness beyond this dark spot. Also, dilution of the penetrant material is not necessary using the "meniscus method," thereby variables of dilution are eliminated. However further development of this

method as well as alternative test methods for measuring fluorescence intensity are needed and are being investigated.

Standard Metal Specimen of Known Surface Characteristics

Proper evaluation of penetrants and adequate testing procedures depend greatly on the test specimen used. Standard test specimens should be easily prepared, reproducible, and possess defects of uniform depth and width.

Some of the more common test standards currently popular will be discussed below:

Quench Cracked Aluminum Block

The cracked aluminum block test specimens are suitable only for comparison purposes. They are a useful guide in determining whether penetrant "A" is better or worse than penetrant "B" for general use. Also, a check on technique can be accomplished through the use of aluminum block specimens.

Crack patterns produced on aluminum blocks are neither uniform, nor of controllable size; and, the dimensional distribution is rather broad.

Test specimens are panels three inches long by two inches wide cut from $\frac{5}{8}$ inch 2024 aluminum. Each block is heated over a gas burner to a temperature of 950°F. The temperature is determined by using Tempilaq by coating an area the size of a penny with the Tempilaq, which sensitizes the block. The block is quenched immediately in cold water after reaching the desired temperature to produce cracks in the block. A slot $\frac{1}{8}$ inch wide by $\frac{1}{8}$ inch deep cut in the two-inch direction across the center of the heat affected zone forms two similar specimens thus eliminating cross contamination during the penetrant comparison. Figure 7 is a photograph of an aluminum test specimen treated with a penetrant.

Magnesium Sheet Strip Test Specimens

The magnesium sheet test specimen is produced by bending an AZ-31 magnesium alloy sheet. Cracks are formed at the tension side of the bent sheet in the parallel direction to the bending stress. Flaw indications produced in this test specimen also are not uniform and are not controllable.

Brittle Metallic Plating Specimen

Another specimen may be produced from a strip of polished ductile iron. A brittle layer of iron is deposited onto the surface electrolytically and cracks are induced by thermal stress or bending. The cracks extend across the width of the plate and are parallel to each other. Such cracks are extremely narrow as well as quite small; therefore, they are not easily shown by the penetrant method.

The critical characteristics of test specimens of this kind are dependent upon two factors—the thickness of plating and the curvature of bending. Plates more than 0.2 mm thick are required to obtain line flaw indications. Test pieces with plate thicknesses of 0.25, 0.5, and 1.0 mm were prepared and placed on the bending device shown in figure 8. The bending curvature was varied by changing the displacement of the load head. Test results indicate that the larger the bending curvature and the thinner the plate, the more

minute the cracks will become. However, micro-cracks close to the detection limits of fluorescent penetrant testing are very difficult to produce by this method.

Pressure Type Fixture as a Standard

A more controlled test involves the use of a pair of highly polished blocks which are pressed together on top of each polishing surface; the gap between the surfaces is to represent the defect. The advantages of this procedure are that the size of the defect is controllable simply by regulating the pressure applied; also the fixture is readily disassembled after use. The major disadvantage is that when two ground metal surfaces are pressed together, the mating surfaces deform as the pressure increases and the gap representing the defect loses some of its characteristics. Figure 9 shows a pressure type fixture used in penetrant testing.

Chromium Electroplates

Work being done on the production of chromium electroplates of known crack geometry is promising. It is known that under controlled conditions of current density temperature and bath composition, chromium plate on nickel base will produce reproducible crack systems.

Plates are produced using 24-gage uniform "blue steel," 3 by 4 inches in size. First, an electrodeposit of nickel is laid down; then a layer of chromium is electrodeposited on top of the nickel. The conditions for electroplating are varied to develop crack systems. Also in this work, a system has been developed for recording the crack pattern. A photographic paper impregnated with dimethylglyoxime is pressed against the specimen surface and electric current is passed through the paper so that the nickel ions migrate through the cracks and deposit in the paper as a red precipitate of nickel dimethylglyoxime.

Test runs of these plates indicate that if the plating bath temperature is not closely controlled, a wide range of crack counts will be observed. When temperature is controlled within close limits, the crack counts (number of cracks per linear inch) are independent of plate thickness in the thickness range from 80 to 400 micro inches. At $113^{\circ} \pm 2^{\circ}\text{F}$, the crack count is in the range of 440 to 525 cracks per linear inch over a range of plate thicknesses of 80 to 400 micro inches. These results indicate that the crack count of a chromium electroplate is directly dependent on plating bath temperature. To investigate further the effect of temperature, crack counts may be obtained also by direct microscopic observation, with another series of plates (see figure 10).

Other variables being investigated such as plate thickness and plate age, will influence the crack count of a chromium plate. Tests indicate that there is an increase in crack count as the plate thickness increases from 855 to 117 micro inches. For thickness above 150 micro inches, the crack count does not change appreciably.

CONCLUSIONS

Although the penetrant process of inspection has been in use for many years and has become a standard procedure in testing structural parts for surface defects, we are only now discovering, through investigations of its chemical and physical properties, how a penetrant works. Yet, much work is left to be done. Correlation studies of the physical properties of penetrants with the results of tests using standard test specimens with known crack geometry, and establishment of proper relationships between detection sensitivity and testing procedure are only two of the many problems left to be solved.

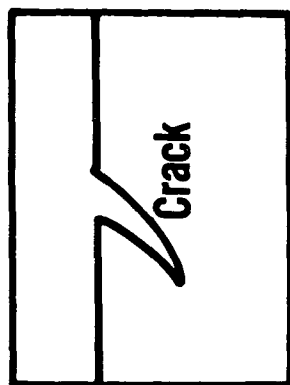
Some assistance in this direction may have been contributed by results of the theoretical study and experimental investigations discussed in this report which lead to the following conclusions:

1. It is possible to control accurately the sensitivity of penetrant systems to almost any desired level of inspection, and
2. Direct comparisons between penetrants for full advantage of detection sensitivities may be accomplished by using standard test specimens of known surface characteristics and by confining dimensional distribution of defects within a narrower range than that found in other test standards.

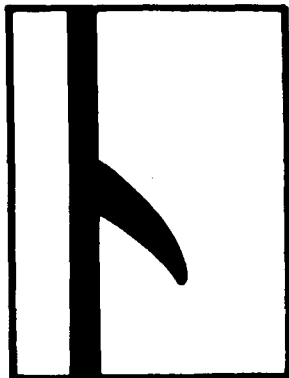
REFERENCES

1. McMaster, Robert C., Nondestructive Testing Handbook, Edited for the Society for Nondestructive Testing
2. McCauley, R.B., and Van Winkle, Q., "Research to Develop Methods for Measuring The Properties of Penetrant Flow Inspection Materials." The Ohio State University Research Foundation
3. Alburger, J.R., "Brightness, Stability, and Sensitivity in Shannon-Glow Fluorescent Penetrant Systems." The Alban H. Reid Foundation for Physical Research.
4. Third International Conference on Nondestructive Testing, "The Standardization of Magnetic Particle and Penetrant Testing." Keynote Paper No 24.
5. U. S. Department of Commerce, "Penetrant Inspection." Quality Control Digest, No. 2, November 1959.

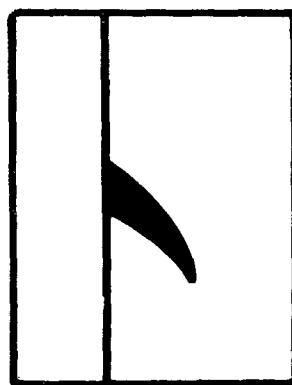
MECHANISM of PENETRANT FLAW DETECTION



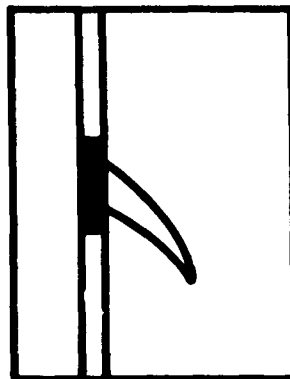
Cleaned Surface



Penetrant Covered



Excess Penetrant Removed

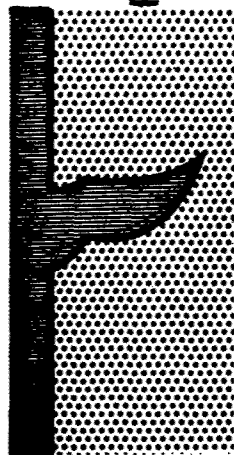


Developer Applied

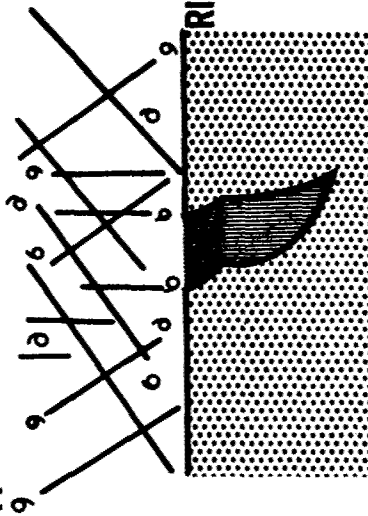
Figure 1.

ONE-STEP PROCESS

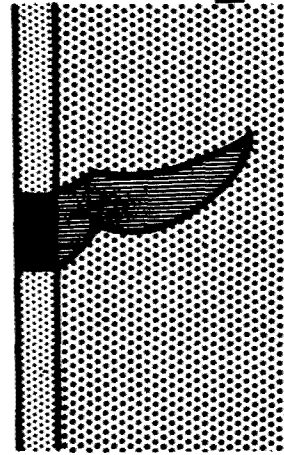
WATER WASHABLE PENETRANT



PENETRATION - Penetrant On Surface Seeps Into Crack



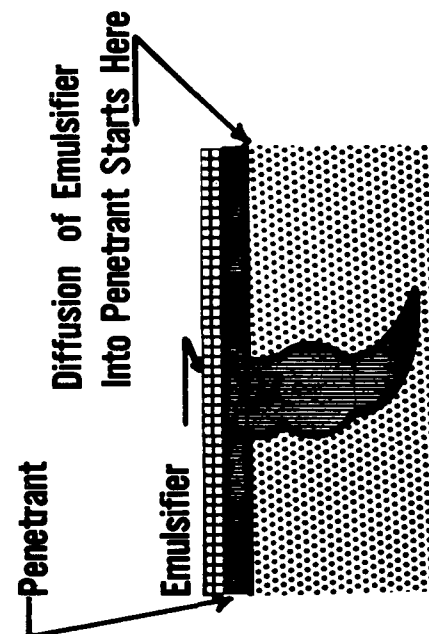
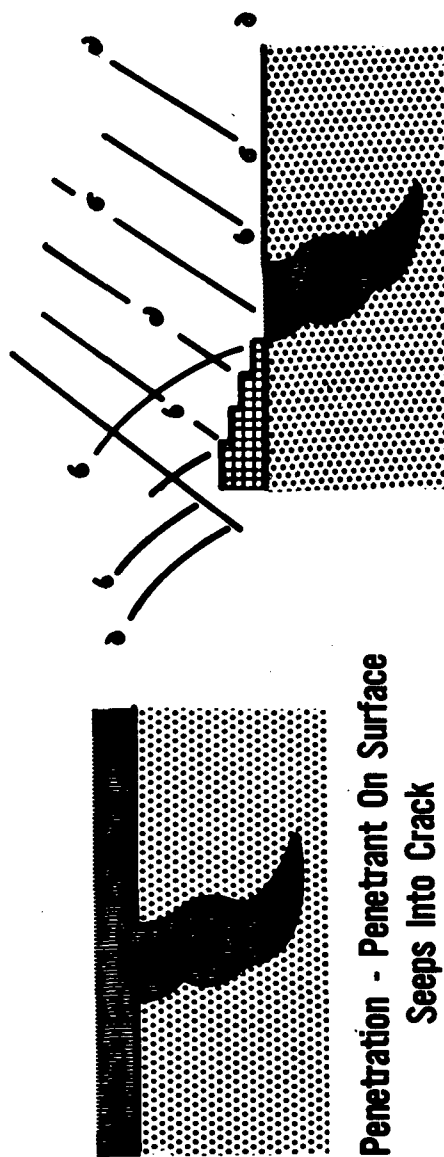
RINSE - Water Spray Removes
Penetrant From Surface But
Not From Cracks And Pores



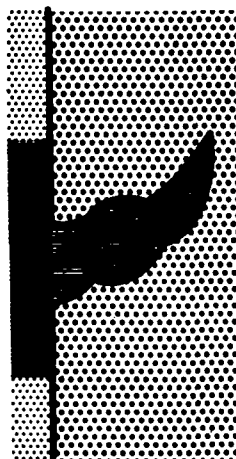
DEVELOPMENT - Developer Acts Like A Blotter
To Draw Penetrant Out Of Crack

Figure 2.

TWO-STEP PROCESS - POST EMULSIFIER PENETRANT



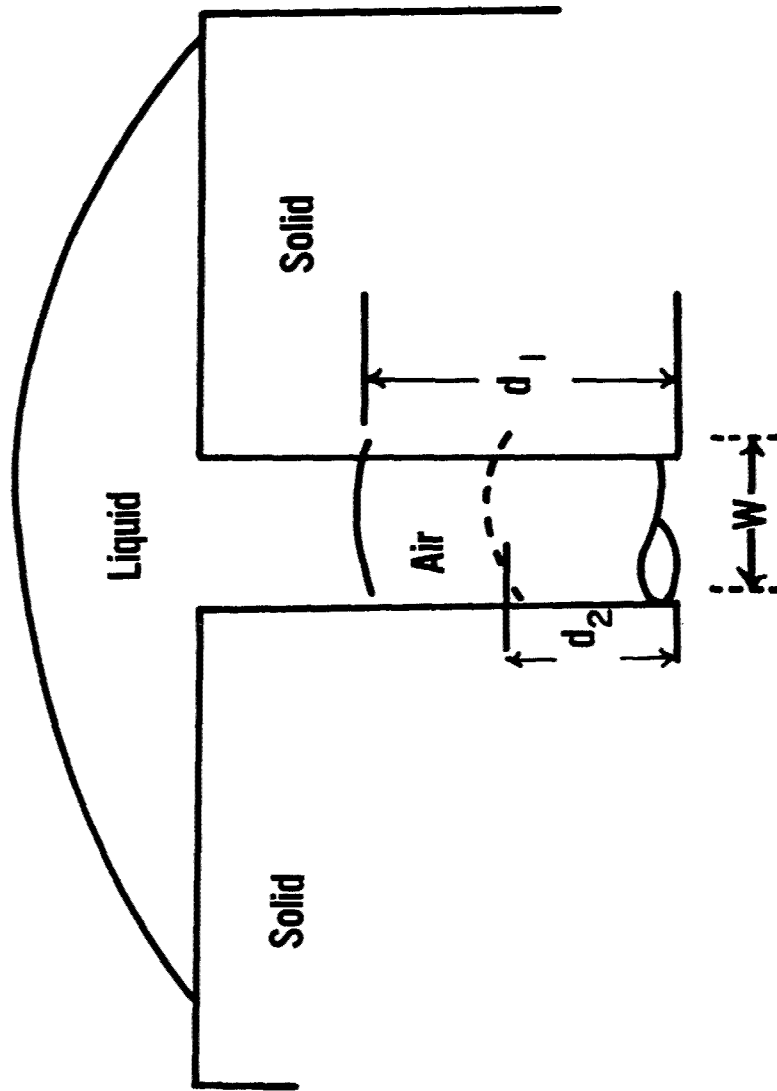
Water Spray Removes Emulsified Penetrant



Development - Developer Acts Like A Blotter To Draw Penetrant Out Of Cracks

Figure 3.

IMMERSIONAL WETTING IN CRACK PENETRATION



d_1 = Air Column At Pressure P_1

d_2 = Air Column With Increased Pressure P_2

Figure 4.

EXPULSION of AIR FROM A CRACK THROUGH CRACK WIDTH VARIATION

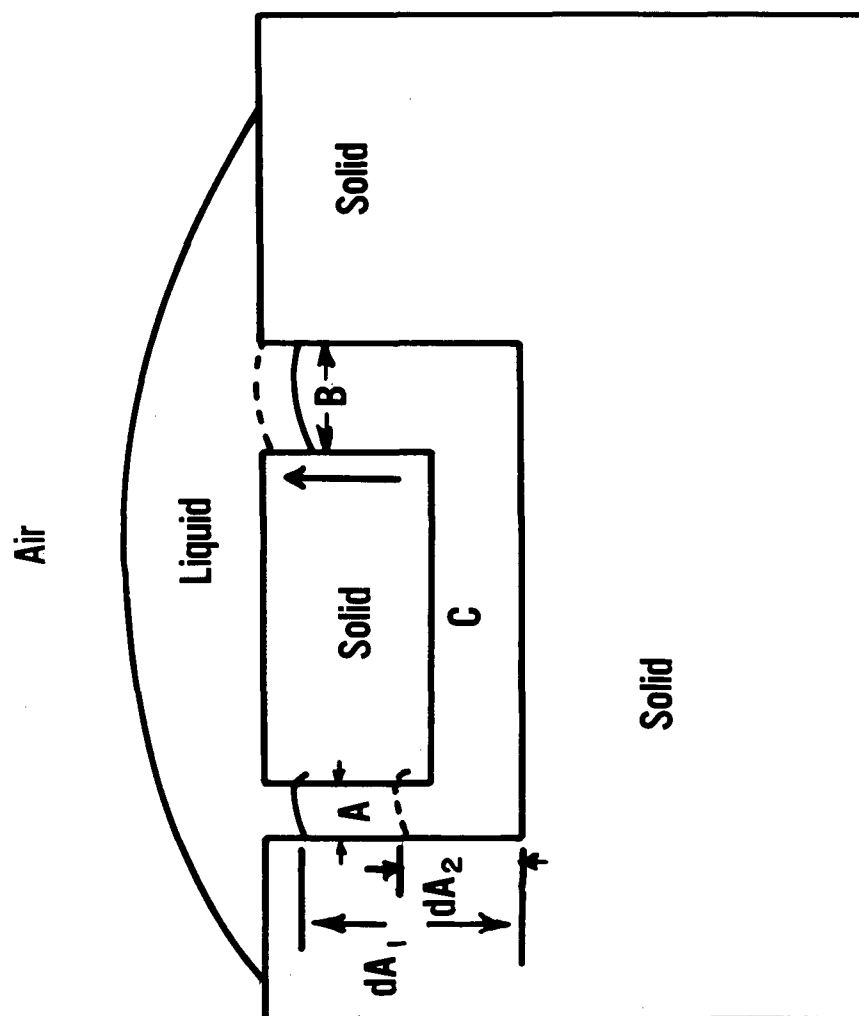


Figure 5.

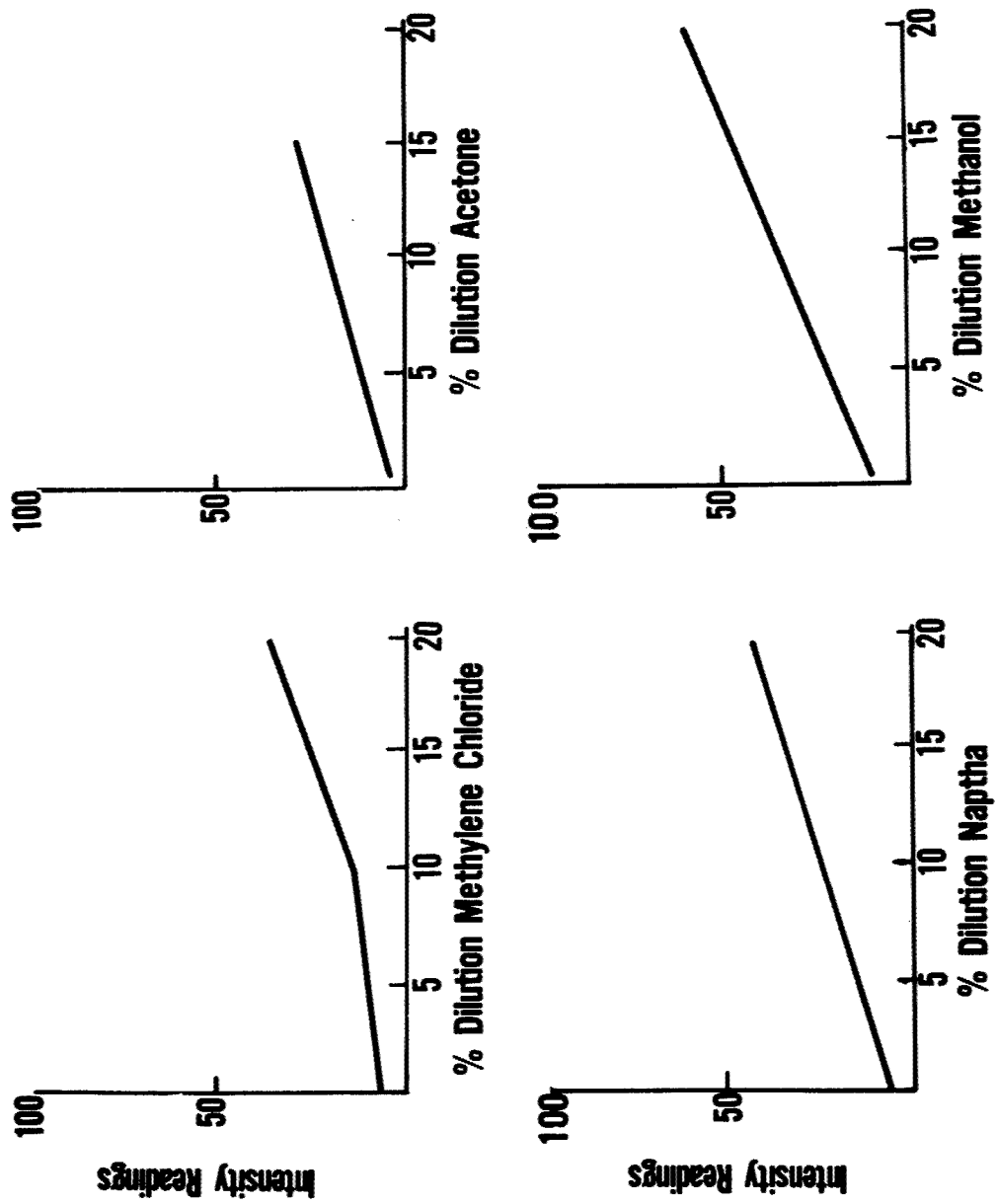
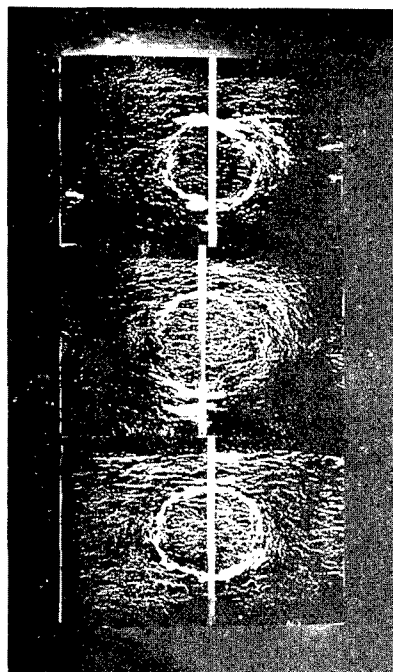
DILUTION of PENETRANT F-401

Figure 6.

CRACKED ALUMINUM BLOCK WITH INDICATIONS

Fluorescent Penetrant Indication



Visible Penetrant Indication



Figure 7.

BENDING DEVICE

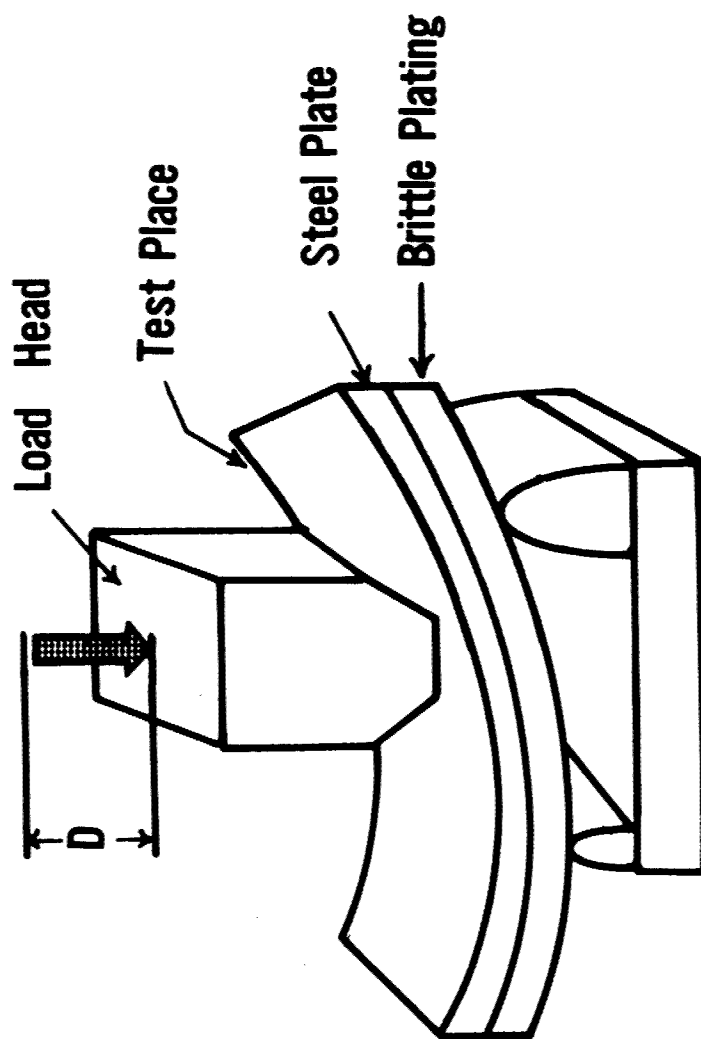


Figure 8.

PENETRANT TESTING JIG

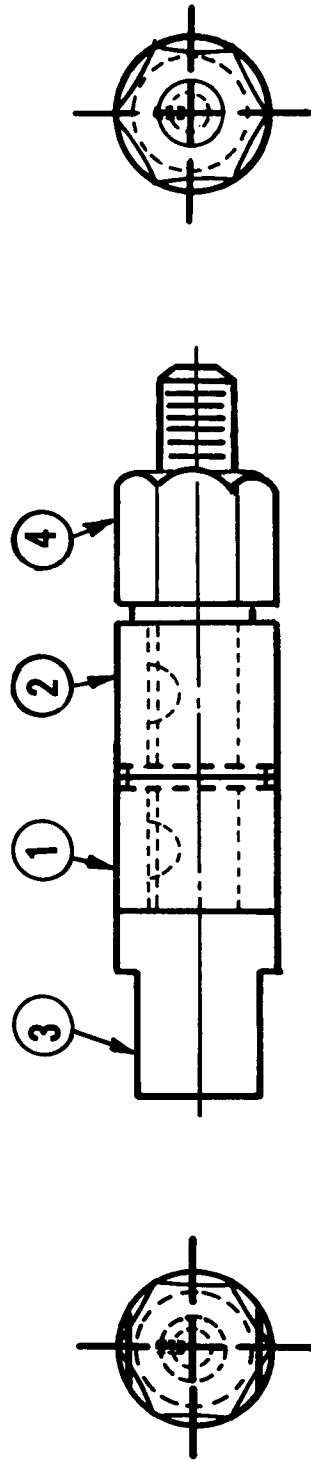


Figure 9.

CRACKS PER LINEAR INCH VS. PLATING TEMPERATURE

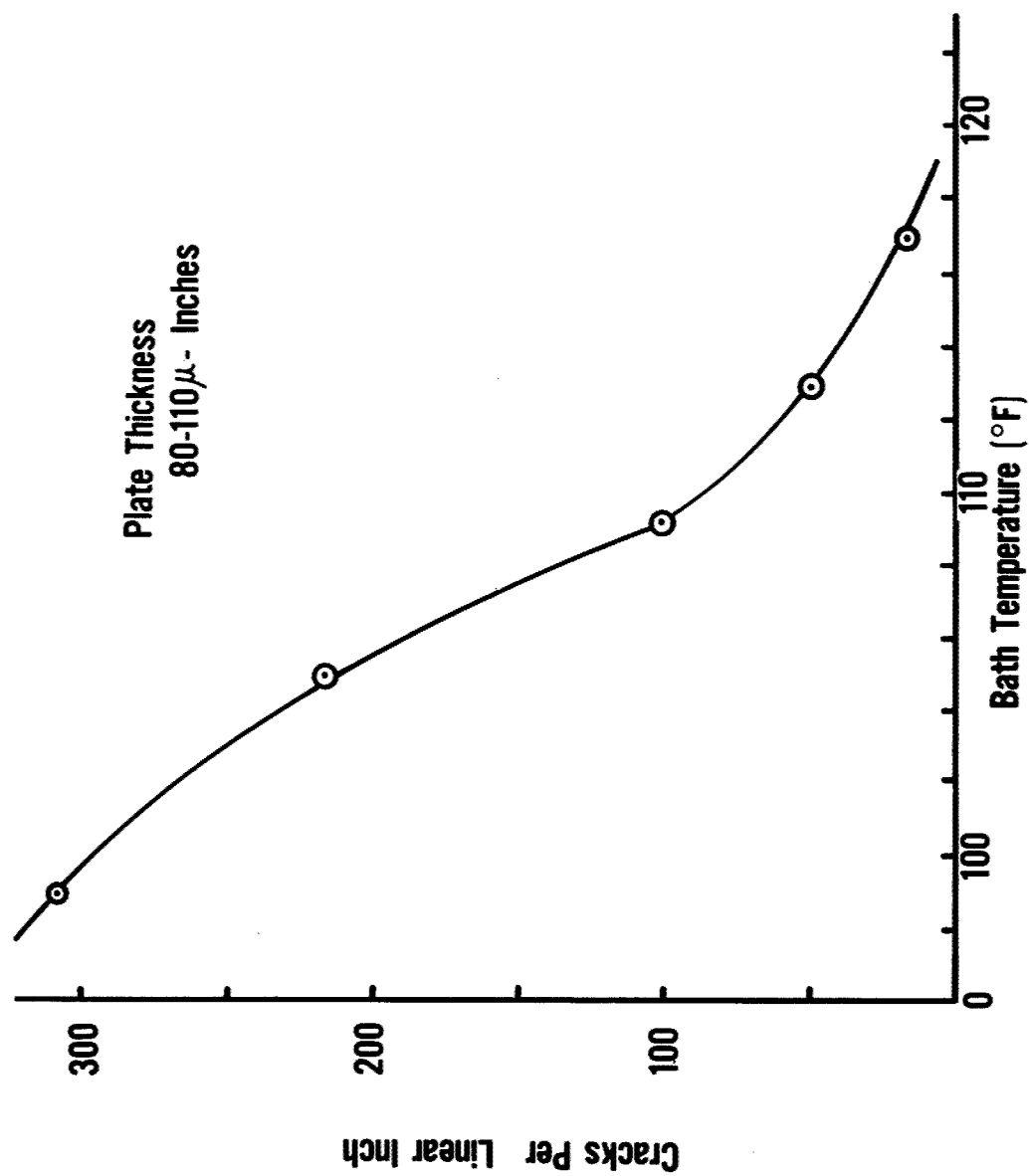


Figure 10.

ABLATION MATERIALS

Chairman

Mr. H. S. Schwartz

Speaker

Mr. D. L. Schmidt

Panel Members

Lt. L. Hjelm

Mr. R. Harned (BMD)

Lt. W. Jones

Mr. D. Hart (Edwards AFB)

ABLATIVE MATERIALS

Donald L. Schmidt

Directorate of Materials and Processes, ASD

Introduction

Advances in aeronautics and astronautics have been closely associated with significant increases in operational temperatures. In chemical combustion systems, flame temperatures are approaching 5500°F and higher. Gas temperatures at least twice that high are being encountered in the boundary layer of hypersonic atmospheric entry vehicles. These extremely high temperature conditions may lead to thermal destruction of an exposed vehicle or a component, unless suitable protection is provided.

Protection of a structure in a very high temperature environment may be accomplished with ease through the use of a new class of engineering materials. These thermally protective materials are known as "ablaters" or "ablative materials". They are applied to the exterior of a load bearing structure and thereby isolate it from the hyperthermal environment. The structure is thus maintained near its initial temperature, at which it exhibits optimum strength characteristics.

Ablative materials are unique in that they accommodate virtually any temperature or heat flux condition, automatically control the surface temperature, greatly restrict any internal flow of heat, and expend thousands of Btu's of energy for each pound of material. These capabilities are the result of a self-regulating, orderly and gradual removal of exposed surface material, which takes place during interaction of the high temperature environment with the material.

Ablative Process

Materials ablation in high temperature environments is a subject of great complexity, and as a consequence is not too well understood. Certain chemical and physical aspects of the process have been identified, however, and they shall be given for the case of an ablating vitreous fiber reinforced plastic. Initially, heat incident to the surface is absorbed and then conducted into the material substrate. Heat penetration proceeds at a low rate, due to the very low thermal conductivity of the ablator. The surface temperature thus rises rapidly, and thermal degradation begins in some form. Organic components of the composite vaporize into numerous gaseous products of varying molecular weights, often leaving behind a residual char layer. Thermochemical and mechanical attack of this porous carbonaceous structure results in surface recession, thus exposing the reinforcing fibers to the hot gas stream. Fusion of the fibers occurs and the molten material covers the surface either as a film or as droplets. This melt is partially vaporized, and the remainder is convected along the surface under the influence of the external forces of gas pressure and shear.

Ablative degradation of the reinforced plastic is illustrated in figure 1. Damage to the material is noted in four distinct layers. First, surface material has been removed by the combined action of thermal, chemical and mechanical effects. On the ablated surface is a thin film and several droplets of melted glass, which have been formed from the reinforcing fibers. Under this surface layer, a porous carbonized material reinforced with residual glass fibers is evident. The volatile-loss layer is adjacent to the char layer,

and has been designated as such because of the slight loss of organic resin. The virgin material lies beneath these damaged zones, and has experienced little or no rise in temperature.

Thermal Parameters of Ablation

During high temperature exposure, an ablative material is generally able to absorb, dissipate and block between 500 to over 10,000 Btu's for each pound of material. This phenomenal capability is due to the various thermal accommodation parameters which function during material ablation. These parameters are shown in figure 2. Sensible temperature rise of the ablator and its pyrolytic products accounts for some heat absorption the magnitude of which is generally small. Additional heat is expended by chemical reactions of the thermally degrading material, such as cleavage of chemical bonds. Various endothermic phase changes take place. Some of these energy absorbing processes are depolymerization, melting, vaporization, sublimation, and others. A small amount of energy may be transported to another physical location by mechanical shearing of solid material from the ablating surface. Likewise, any surface melt on the ablator may be removed by imposing forces of the environment. Gases formed in the material substrate are heated to a higher temperature as they percolate to the surface. Due to their high heat capacity, they are able to absorb a large amount of heat by sensible temperature rise. The newly formed gases are ejected into the adjacent boundary layer greatly reducing the effective temperature level of the environment. Consequently, less heat is transferred to the ablating surface. Energy is dissipated by surface radiation, with the rate of heat transport depending upon the temperature and emittance of the ablator. Additional heat will be radiated into the material substrate, provided the material is radiation transparent or semi-transparent.

The amount of heat expended by each of the above processes depends critically upon the nature of the heating environment and the material being considered.

History of Ablators

The first known ablative materials were meteorites. These thermally degraded bodies coming to us from space were indeed a subject of great curiosity, since they had demonstrated in principle the utility of aerodynamic ablation for thermal protection of atmospheric entry objects. Perhaps in these bodies were hidden the secrets to successful re-entry of man-made vehicles. Research was thus initiated to discover their composition and construction. Information obtained was interesting, but it provided few usable clues. Furthermore, it was apparent that the stony and iron meteoritic materials were not suitable for application to man-made thermal protection systems. Hence, the search for workable ablative materials was continued.

Man-made ablative materials were discovered only a decade ago. Various techniques were being explored to protect and insulate structural metals while exposed to a hot rocket exhaust. Certain reinforced plastics and ceramics were seen to exhibit remarkable durability during short time hyperthermal exposure. In addition, the high temperature of the environment was restricted to the surface region of the ablating material. These thermal barrier materials apparently had great potential for solving the high temperature problems associated with re-entry heating and rocket propulsion systems. In the next several years, thousands of different material compositions and constructions were characterized and evaluated on a trial-and-error basis. The high temperature facilities used were various combustion torches, small rocket motors, arc plasma jets, pebble bed heaters, arc imaging furnaces, and others. Environmental simulation was often impossible

to obtain with these facilities, but their use permitted the generation of test conditions in which much useful materials information was obtained. Meanwhile, ablative theories were being formulated and experimentally verified. These theories helped to explain materials behavior at very high temperatures, and provided some guidance for their engineering application. Various types of materials were investigated, and plastics and ceramics in homogeneous and composite compositions were found most promising. Composite construction was the most versatile, since the unique properties of individual components were incorporated into a single material system. Furthermore, it was possible to adjust these material components to obtain the desired balance of properties and to tailor them to a specific environment. By these trial-and-error and systematic materials investigations, a wide variety of ablative materials have been identified. Many of these materials are shown in table 1.

TABLE 1

ABLATIVE MATERIALS COMPOSITIONS

Homogeneous Ablators	Composite Ablators
Plastics	Reinforced Plastics
Polytetrafluoroethylene	Organic resins reinforced with various fibrous materials, such as glass fiber reinforced phenolic
Polyethylene	
Polyamides	
Phenolics	
Modified epoxies	Reinforced Ceramics .
Expanded (foamed) resins	Ceramic filled metal honeycomb
Carbonized resins	Metal fiber reinforced ceramic
Ceramics	Impregnated Systems
Fused silica	Organic resin filled porous ceramic
Zirconia	Inorganic particle filled refractory
Magnesia	
Expanded (foamed) ceramics	

This list is not an all inclusive one, but it identifies materials which have exhibited relatively good performance in several different hyperthermal environments.

Advantages and Limitations

Ablative materials have been widely used in heat protective systems of hypersonic atmospheric vehicles, rocket propulsion systems, various thermal barriers, and other high temperature applications. This extensive acceptance in aerospace systems is due to the unique combination of properties and characteristics offered by the materials. Figure 3 lists the major advantages of ablative materials, and their twofold limitations.

Ablative materials absorb and dissipate high heat loads with minimum surface erosion, and provide excellent thermal insulation of the substrate. They have no upper service temperature limit, and they can accommodate virtually any operational temperature by controlled material degradation. They are usually light and vary from about ten pounds per cubic foot for foamed plastics to over two hundred pounds per cubic foot for metal fiber reinforced ceramics. Organic ablators inherently possess good resistance to both

thermal and mechanical shock, but ceramic ablators are shock sensitive. This material deficiency has been greatly reduced by the use of fiber or honeycomb reinforcements. Ablative materials are readily available and are non-strategic. Their relative costs are low. Designing with ablative materials is not any simple task, but it certainly involves less complexity than with other thermal protection schemes. Lastly, ablative materials degrade in a self-regulating and orderly manner, thus eliminating any requirement for an actively controlled cooling system.

The thermal efficiency and effectiveness of an ablator is reduced with increasingly higher mechanical forces. A second limitation of these materials is their service time dependency. Optimum performance is generally obtained for minutes of operation or less, with reduced performance with increasing exposure times.

Ablative Performance

The performance of an ablative material is a complex function of both materials and environmental variables. Since the design spectrum of hyperthermal environments is very large, it is impossible for a single material to be optimum for all types of environments. Each material exhibits optimum performance characteristics for a specific environment, and may even become unusable in other high temperature environments. It thus becomes necessary to develop a wide variety of ablators, which have the collective capability to accommodate the entire design spectrum of hyperthermal environments.

A proper balance of materials properties and characteristics leads to optimum ablative performance. Important materials variables are shown in figure 4, together with the desired property trend. It is noted that the empirical heat of ablation value should be as high as possible to minimize the weight of material required to accommodate the incident flux. The strength of the intact ablator and its residual surface material should also be high, and adequate to withstand the imposing mechanical forces of the environment. Other materials properties which require high numerical values include: the enthalpy of phase changes, specific heat and thermal shock resistance. A low thermal conductivity is desirable for obvious reasons of insulation. Low density materials are generally optimum, provided they can accommodate the imposing forces of the environment. The dimensional erosion of the surface should be relatively low, uniform, and predictable. Gaseous species formed by material degradation should be of low molecular weight, a factor which leads to optimum transpiration cooling. Surface emittance should approach unity for maximum heat dissipation. Materials that gasify completely exhibit excellent heat blockage; therefore, all of the initial solid material should be converted to gaseous products. Certain other properties and characteristics of an ablator interact strongly with other materials, environmental and design parameters. Consequently, no general trend for optimum performance can be given. To illustrate, a high ablative temperature is generally desired for conditions involving a very high heating rate. The converse is true for a low heating rate environment.

Environmental variables and their magnitude greatly influence the behavior of an ablator. In figure 5, the important thermal, mechanical and chemical aspects are given for a high temperature environment. Their exact numerical value is dependent upon the specific application and body location being considered. To further complicate the problem, many of these environmental variables may change constantly in a given application (as a nose cone re-entering the earth's atmosphere).

When the mode of surface heating is primarily convective in nature, the ablative material should form a large volume of gas to block the incident flux. If radiation is the predominant

mode of incident heat transfer, the ablating surface should exhibit good reflection characteristics or possess a high emittance for maximum re-radiation. The instantaneous flux and its variation with exposure time must also be considered, since it may be desirable to use a "graded layer" ablator instead of a homogeneous and uniform material. The total heating time dictates the amount of material required for ablative and insulative purposes, and often means lowered material performance with increasing exposure times. Mechanical forces of pressure, shear, vibration, acceleration and deceleration are detrimental. High pressures tend to crush the thermally weakened surface material, and gas shear may erode away solid and liquid materials. Vibration accelerates removal or detachment of the ablating material. Unpredictable problems may be introduced by forces of acceleration and deceleration. For example, molten material on a highly decelerating re-entry heat shield may move in the direction of the apex (opposite to the direction of the gas stream). Thus, first order changes of the heat shield geometry may occur with associated effects on the aerodynamics of the vehicle. Chemical reactivity of the environment is also extremely important, since it may affect the mechanism, thermodynamic and kinetics of the ablative process. To illustrate, oxygen present in the environment accelerates material ablation by oxidation of carbonized systems. It has little effect on molten oxide ablating surfaces.

To summarize, the ablative performance of a material may be altered by many different environmental variables. Careful consideration should therefore be given to each of these factors in determining a materials performance, and in selecting an ablator for a specific high temperature environment.

Research Programs

Although great advances have been made in ablative materials technology, our understanding of these materials in very high temperature environments is inadequate. Numerous problems continue to plague us thereby restricting new developments. Some of these important problem areas are under research by the Air Force and its contractors. In figure 6, the categories of research activities are listed. Each is discussed in detail in this paper.

Ablation Theories

Since materials ablation is a very complicated process, theories are necessary: to obtain additional insights and a better understanding of the process; to identify the materials physical and chemical properties of importance; to predict performance; and to guide future materials research.

Theoretical models have been formulated for the various classes of ablators, and mathematical formulas are available to express their performance. These ablative models have proven to be helpful in predicting material performance, but they require further refinement to extend their utility. At the present time, they contain temperature-dependent thermophysical properties of the ablator which likely are unavailable in the literature. Kinetic expressions may be used in the formulas, some of which are difficult to measure or compute. Lastly, they may contain ill-defined quantities, such as the heat of chemical reaction for an ablating polymeric material.

Theoretical research on ablative materials is presently concentrated on composite systems. Formulas are being developed to express the steady-state temperature distribution in the material substrate, instantaneous char layer thickness and charring rate, and heat of ablation as functions of both materials and environmental variables. Internally ablating

composites are being intensely studied. This type of material system is represented by a porous refractory ceramic skeleton impregnated with a thermally unstable organic resin. The impregnant vaporizes during heating and flows out of the porous skeleton. In so doing, the vapors cool the surface and maintain its dimensional stability.

Mechanisms of Ablation

Ablative materials programs to-date have been primarily of the engineering type, with little regard for the detailed mechanisms by which these ablators are thermally degraded. To fill this void and to provide a fundamental understanding of material ablation, various specialized studies have been initiated. They have generally been concerned with identifying the important physico-chemical aspects of ablation, thermodynamics and kinetics of material reactions, and the influence of both materials and environmental variables on the modes of ablation.

Ablative mechanisms are deduced from research information obtained on the individual reactions and processes of a thermally degrading material. The thermodynamics and kinetics of reactions taking place are analyzed from a theoretical standpoint. Chemical reactions of importance are thus identified, and later studied in detailed investigations. Some of these studies relate to the rate and mode of material decomposition, chemical and physical reactions of the newly formed gaseous products, interactions between the pyrolytic gases and the residual ablative surface, and reactions between the atmospheric constituents and the ablative products. Vacuum pyrolysis and thermogravimetric analysis have been helpful in obtaining the rate of material loss as a function of increasing temperature. Chemical reactions occurring within the material, on the surface and in the boundary layer are followed by such analytical techniques as mass spectrographic analysis, emission spectroscopy, elemental chemical analysis, X-ray diffraction, and others. Energy exchanges accompanying these reactions are being investigated with differential thermal analysis (DTA). Transient species and final gaseous products coming from the ablating surface are identified and quantitatively measured with a time-of-flight mass spectrometer. For carbonizing ablators, electro-thermal analysis is used to follow the conversion of organic material into residual carbon. Residual products contained on the material surface after exposure are analyzed for chemical composition, physical structure, crystallinity, porosity and pore spectra, density changes, strength properties and related material characteristics. The effects of the individual components of the atmosphere on ablative materials are being reviewed. Pure thermal effects on ablators are being investigated with thermal radiation from an arc imaging furnace. Gaseous plasmas similar to those of very high temperature boundary layers are produced with a radio frequency discharge tube. Their mechanism of free radical attack on material surfaces are being researched. For simultaneous simulation of thermal, chemical and mechanical effects, an electric arc plasma jet has proven to be very useful.

From these studies on the mechanisms of material ablation, it has been possible to categorize the ablative modes. These are: simple melting (like an inorganic ceramic), sublimation (such as polyethylene), melting-vaporization (like a resin reinforced plastic), and carbonization-vaporization (such as a phenolic resin). A voluminous amount of information has been obtained. For example, it has been determined that the rate controlling ablative mechanism of a carbonized plastic in high temperature air is primarily that of oxidation. For the case of ceramic oxides in high temperature air, material ablation is controlled predominantly by melting and vaporization processes. As new knowledge is generated on the mechanisms of material ablation, greater control over the ablation process may be exercised to increase heat absorption and insulation.

Elimination of Material Deficiencies

Major emphasis in this area of materials research is devoted to improving the structural characteristics, dimensional stability and useful service life of ablative materials.

The thermally weakened surface layer on an ablating material can be made stronger by reinforcement with a suitable refractory fibrous material. Good results have already been achieved with fibers of silica, zirconia, carbon, graphite, tungsten and other compositions. Significant improvements in the ablative characteristics of ceramics have been obtained with the use of refractory metallic wires, meshes and honeycomb. A second promising concept for improving the structural properties of an ablator concerns the "in situ" synthesis of a refractory on the surface during hyperthermal exposure. This approach utilizes the heat and pressure of the environment to effect the desired reaction. For example, a composite of organic resin and quartz reinforcing fibers will form carbon and molten silica during intense heating. These two products of pyrolysis may react endothermically to form a surface refractory of silicon carbide. However, techniques have to be satisfactorily worked out for maintaining the newly formed carbide on the ablating surface.

Improvements in the dimensional stability of ablative materials is being pursued from three different technical approaches. The first concept under exploration concerns proper orientation of the reinforcing agent in an ablative composite. It has been shown that fibers perpendicular to the exposed surface invariably result in a minimum rate of linear ablation. Intumescent ablators (swell in response to heating) offer another interesting approach to the development of dimensionally stable materials. For example, thermal exposure of certain modified epoxies results in a plastic char which has a tendency to swell. Material loss at the surface is thus compensated dimensionally by internal swelling of the carbonizing plastic residue. Internally ablating composites offer a third solution to the problem of dimensionally stable ablators. Excellent results have been obtained with porous skeletons of refractory oxides impregnated with non-carbonizing resins. The original dimensions of the ablator are assured by continual surface cooling with internally generated gases.

Efforts are underway to extend the service life of ablative materials. An obvious approach is to maximize the heat of ablation value, the insulation index, or both. Material compositions with heats of ablation approaching those of graphite, but with better thermal insulation are being studied. Superior ablative insulators are required for long time exposures, such as satellite re-entry heating. Most ablators behave primarily as a heat sink in this type of environment, and have poor insulative qualities. In order to force the ablative process in low heating rate environments, materials are required to undergo extensive depolymerization and vaporization at temperatures of 1000°F or lower. New long chain, non-carbonizing plastics of this type have been synthesized, and used successfully for up to 10 minutes in simulated satellite heating conditions.

Several of the new ablative compositions have been found to be semi-transparent to radiation from the environment. Heat is thus transferred into the material substrate with an associated increase in its internal temperature. New thermal barrier concepts for these materials have recently been proposed, and they are being reduced to practice. Some of these approaches are: incorporation into the ablative material of embedded scattering particles, absorbing substances, foil reflectors, and multilayer dielectric reflectors.

Synthesis and Formulation

Numerous research programs are devoted to the syntheses of new material compositions and constructions. Organic and inorganic polymers with high endothermic capacity are being created by: modification of conventional polymeric structures, copolymerization of available resins, and synthesis of new polymeric matrices. There is a primary interest in the high-carbon aromatics, metalloxanes, triazines, polyazaporphyrins, organo-metallic chelates, borazoles, and other polymeric systems. Flexible polymers with high carbonization potential are being synthesized for use as rocket case liner materials. Two notable achievements have been reported in this area. They are the synthesis of castor oil modified epoxies and the incorporation of elastomeric polymers into the phenolic resin structure.

Resinous materials which are inexpensive, castable, and cure at room temperature are the object of current materials research. Excellent results have been obtained with modified epoxies and those filled with various carbonizing particulate matter.

Considerable research effort is being devoted to the synthesis and development of refractory fibrous materials, which exhibit good thermostructural properties for reinforcement of ablative matrices. Primary interest is centered on compositions of refractory metals, graphites, carbides, oxides, nitrides and borides. Fine diameter fibers of tungsten, tantalum, molybdenum, titanium, and zirconium have been prepared for incorporation into ablative ceramic and plastic composites. Successful synthesis of the following materials have been reported: long fibers of quartz, zirconia and elemental boron, short length crystals of alumina, titania, and thoria, and very short length whiskers of silicon carbide, pyrolytic graphite and beryllia. Refractory carbon and graphite fibers have been made by conversion of synthetic organic fibers under conditions of high temperature and vacuum. These fibrous materials have exhibited extremely high sublimation temperatures and increasing strength with elevated temperatures. Their uses to date have been limited by a relatively low strength, oxidation at high temperatures, and a moderately high thermal conductivity. Successful synthesis of long metallic carbide fibers appears likely within the near future. When available, these non-melting fibers will be widely used in ablative composites.

Particle fillers of various chemical composition and sizes are being studied as possible additives in ablative composites. Their purpose is generally a highly specialized one, such as to increase the surface emittance and temperature, alter the viscosity and surface tension of the inorganic components, generate a large volume of low molecular weight gases, increase the endothermic absorption of heat, and other functions. Several problems have been encountered with their use, such as an undesirable influence of the filler on other ablative reactions, uncontrolled degradation of the particle, and loss of the particle from the surface before it performs its intended function.

Ceramics are receiving increasingly greater attention as potential ablative materials, since their tendency to spall and thermally fracture have been overcome by the use of suitable reinforcing agents. Pure and mixed oxides of zirconia, thoria, magnesia and hafnia are being formulated for use as bulk ablators or as coatings for other materials.

Formulation and fabrication of ablative composites have been progressing rapidly. Metallic, ceramic and plastic elements have been successfully incorporated into single material structures, and maintained as a unit during hyperthermal exposure. An example of this type of multilayer construction is shown in figure 7, which is a photograph of an entrance cone of a test rocket nozzle. The internal surface is an arc plasma sprayed

tungsten coating, the purpose of which is to provide short-time thermal protection by delaying the internal heat transfer. This metallic coating is diffusion bonded to a substrate insulative layer, which is itself composed of a porous zirconia foam reinforced with stainless steel honeycomb. The external load bearing member of the composite is a silica fiber reinforced plastic, adhesively bonded to the reinforced ceramic layer. This type of construction has successfully withstood a solid propellant firing involving a flame temperature of 6800°F.

Materials Characterization

Increased emphasis on materials synthesis and formulation has lead to the generation of many new ablative materials. Considerable burden has thus been placed on the evaluation engineer to determine their ablative characteristics and potential for specific types of high temperature environments. This activity may be costly, time consuming and complex, due to the large number of available materials, and, the environmental aspects which must be investigated. The most satisfactory solution obtained, involves a division of this research into two sequential steps. First, newly synthesized candidate materials are rapidly screened at several standardized test conditions. Obvious ablative characteristics and material limitations are observed, measured and computed. These generally involve: uniformity and rate of ablation, surface characteristics including spalling, internal heat penetration, surface temperature and radiation, heat of ablation, and possibly other performance indices.

Several high temperature facilities have been developed and are readily available for materials screening and characterization studies. These testing devices are given in table 2, along with their performance characteristics, advantages and limitations. The type of facility selected for a particular materials evaluation will depend upon the objectives of the work and the materials research information desired.

Materials intended for re-entry heating environments are rapidly screened in small 50 to 500 kilowatt electric arc-jets. They are generally prepared in the configuration of a flat faced cylindrical rod, and exposed to non-variant test conditions in the arc jet. Figure 8 shows three research specimens after exposure to high enthalpy air from an arc wind tunnel. The most promising materials identified in screening tests are then scaled up into larger models, and evaluated further in highly specialized arc heaters and under carefully controlled conditions.

Materials intended for rocket exhaust environments are screened in a combustion gas device, such as a subsonic or supersonic oxy-acetylene torch. Either cylindrical rods or flat plates are used to obtain general ablative characteristics of the materials. Figure 9 illustrates this type of materials screening, and shows a ceramic ablator being exposed to supersonic combustion products from an oxy-acetylene torch. Promising materials obtained from these comparative materials studies are scaled up into nozzle or insulator sections, and further characterized with small rocket motors.

Nozzle ablative materials have been characterized in a variety of liquid propellant motors, one of which is the hydrogen-oxygen motor. This particular evaluation facility has been widely used, since it generates flame temperatures, mass-flow parameters and gas chemical effects of interest. Candidate materials are fabricated into small research nozzles, in preparation for motor firing. A nozzle specimen is fastened to the end of the motor, as shown in figure 10. Material exposure is accomplished by exhausting the combustion products through the nozzle section. A photograph of a material research nozzle before and after firing is shown in figure 11. Note the throat erosion and surface charring which has taken place in this molded plastic specimen.

Flexible ablators are fabricated into small blast tube specimens and characterized by exposure to a solid propellant flame. Up to eight different materials can be exposed simultaneously, as shown in figure 12. Each candidate material is arranged in a circle about the blast tube section which forms a part of the actual motor wall. In this manner, direct comparative results on various materials are obtained with economy of operation.

Some of the remaining problems to be solved in materials characterization and evaluation are: limited availability and high costs of materials screening devices, limitations in instrumentation for accurate measurement of both environmental parameters and materials response, development of more meaningful indices of material performance, difficulties in identifying the mechanisms and causes of material failure, and the inability to scale up from small research specimens to larger end item applications.

Material-Environment Interactions

As new ablative materials are considered for use in specialized hyperthermal environments, it often becomes necessary to conduct material-environment interaction studies. The purpose of these studies is generally to: identify and quantitatively determine the reactive species present in the environment, elucidate their mechanism of interaction with the ablator, and develop new techniques for inhibiting undesirable reactions.

During hypersonic atmospheric entry, an ablative material is exposed to a very high temperature boundary layer. Gaseous species present in the boundary layer are highly reactive, due to their ionized and dissociated states and their chemical composition. The effect of these gaseous species on ablative materials has been investigated with interesting results. Organic ablators were found to be more susceptible to plasma attack, when compared to inorganic ablative materials. Silicones and other thermosetting resins were more resistant to plasma attack than were the thermoplastic resins. Gaseous oxygen plasma produced a higher rate of chemical vaporization than did the less reactive nitrogen plasma. This effect was particularly evident with ablative materials that formed a carbonaceous surface during heating.

Combustion products from advanced propellants have introduced new chemical corrosion problems for ablative materials. Studies have been initiated on gas-solid, gas-liquid and liquid-liquid reactions, such as those occurring between high temperature water vapor and metallic carbides, fluoride vapors and inorganic oxide melts, liquid aluminum oxide and molten silica, and other suspected deleterious reactions. The chemical kinetics of these reactions are being investigated. Each system has its peculiar characteristics. For example, aluminum particles present in a solid propellant are oxidized to molten alumina in the combustion stream. These liquid droplets may then contact the ablating wall, transfer energy to it, and form a new low-viscosity eutectic which is rapidly swept away by the gas stream. The kinetics of this reaction are governed by such complex factors as: rate of impingement of the alumina droplets, wetting characteristics of the ablating wall, mobility of the alumina phase on the surface and internal diffusion rate, thermochemical state of the surface, and diffusion rate of reaction products away from the surface.

In the future, the chemistry of hyperthermal environments will likely continue to change as new propellants are developed and new planetary atmospheres are explored. It will then be necessary to ascertain the individual effects of the reactive atmospheric constituents on ablative surfaces.

Applications Engineering

Effective and efficient design with ablative materials has seldom been achieved, due to the newness of the materials, lack of preceding similar designs, complexity of the design factors involved, and our incomplete knowledge concerning realistic design criteria. In designing with ablative materials, consideration must be given to the environmental variables and their time dependency, availability and uniformity of candidate materials compositions and constructions, materials properties and characteristics, materials formulation and fabrication, design requirements for thermal, mechanical and chemical properties, safety factors and other aspects peculiar to the design. Some degree of uncertainty exists for each of these factors, and designers have had a tendency to use an overall safety factor rather than one based on the uncertainty of each design criterion. Further research on optimum design techniques for ablative materials is required.

Another serious problem in the application of ablative materials is the frequent inability to use design data obtained on sub-scale models. Certain material components, such as a fiber diameter, are not proportionately scaled up in going to larger end items. Slight differences between the test environment of the sub-scale model and that of the actual end item may lead to significant differences in material performance.

The notable lack of standardized design criteria limits the effective use of ablative materials. Virtually all of the materials performance indices are in some way tied to the boundary conditions under which they were determined. For example, the heat of ablation of a material in an argon test environment may be vastly different from that obtained in an air environment.

Performance indices for ablative materials are not well defined, and this lack of standardization is leading to some confusion. To illustrate, there are many different definitions for the "heat of ablation". Some research is being conducted on refining this material performance parameter, and extending its utility to a greater number of design situations. Presently, only partial success has been obtained.

Properties of ablative materials, which are essential to optimum design, are rapidly being generated. The data are generally determined at equilibrium conditions and at temperatures up to the initial point of material phase change. For lack of available information, designers are often forced to use this data for transient ablative conditions involving considerably higher temperatures. Much of the materials property information given in the literature has limited utility due to the incomplete description of the important materials composition and construction, test environment, and experimental procedures used.

Many new problems are encountered in the fabrication of ablative materials. Few acceptance and rejection standards have been developed. Material and process specifications are virtually non-existent. Expensive and specialized equipment must often be used, such as tape winding machines for oriented woven fiber layups, high pressure presses for large exit cones of rocket nozzles, and vacuum furnaces for material syntheses. Ablative parts are generally made from several dissimilar components, thus requiring suitable techniques for joining them into an integral unit. Nondestructive inspection techniques of ablative parts are required for quality assurance and to improve fabrication techniques. Radiography and ultrasonics have been used with moderate success. Further work is required to identify and classify permissible defects (voids, cracks, matrix-starved areas) in ablative parts, and ascertain their influence on the ablative characteristics. These problems are representative of those faced by materials fabricators and suppliers.

Ablative parts are often subjected to various degrading conditions in the time interval between their fabrication and use in a hyperthermal environment. Some of these possible material degradation factors are: exposure to the elements of the weather, long time storage, handling shock and vibration, contact with chemicals, and similar items. The influence of these items on ablative performance has yet to be determined for many of the ablators presently in use. Further knowledge is required on these potential problem areas to increase the reliability of ablators.

Several Typical Uses

The utility of ablative materials for thermal protection of structural elements has been demonstrated experimentally in a wide variety of laboratory generated hyperthermal environments. Ultimately, it becomes necessary to verify their performance in actual applications: (a) to prove their effectiveness and reliability (b) to confirm theoretical predictions of material performance, and (c) to provide a sound basis for the selection of optimum materials compositions and constructions. Two of the most heralded applications of ablative materials are discussed in detail. These are: re-entry heat shielding and protection from hot rocket exhaust environments.

Hypersonic Atmospheric Entry

One of the most difficult and challenging problems of aerospace flight is the thermal protection of a vehicle as it enters hypersonically into a planetary atmosphere. Unless isolated from this very high temperature environment, the vehicle will likely be thermally destroyed in a manner similar to that of a meteor entering the earth's atmosphere. Research on this critical problem of re-entry heating has led to various workable solutions, such as transpiration and film cooling, radiant cooling, magnetohydrodynamic cooling, solid and liquid heat sinks, and ablative cooling. Of these thermal accommodation techniques, the last two have already been applied successfully to various man-made re-entry bodies. Ablative cooling has achieved the highest degree of success and it has been the most widely used. To-date, ablative materials have thermally protected nose cones of ballistic missiles, orbital entry bodies, and recoverable research vehicles. For the future, ablative materials appear highly promising for use on lifting aerospacecraft and planetary research probes.

Representative uses of ablative materials on atmospheric entry vehicles are shown in figures 13 through 15. Figure 13 is a photograph of an ablative materials research vehicle during launch by an intercontinental ballistic missile. In figure 14, a Discover orbital entry vehicle is shown with its ablative covering. Ablative materials have also been used successfully on manned orbital entry vehicles. Pictured in figure 15 is the Mercury capsule, with its broad, shallow ablative heat shield attached to the extreme forward part of the capsule. The specific ablative materials composition and construction used on these vehicles cannot be reported at this time, since the information is still classified. Nevertheless, it can be stated that each of these re-entry vehicles require different ablative materials because of its respective flight environments. To illustrate, orbital entry heating involving a high enthalpy, laminar flow condition is usually best accommodated with a low temperature, subliming plastic. Turbulent flow conditions and those environments involving high imposed dynamic forces dictate the use of a reinforced plastic or ceramic. The exact ablative material used on a given re-entry vehicle will depend largely on its body location and associated environmental conditions.

Rocket Propulsion Exhausts

The containment and control of hot combustive gases in rocket propulsion systems is necessary for thrust purposes. These propellant gases constitute a severe engineering environment, since they are generally characterized by high temperatures, high mechanical forces, chemical corrosion, and occasionally particle erosion.

Ablative materials have been used successfully in the propulsion systems of both solid- and liquid-fueled rockets. The most notable achievements have been in solid propellant motors, wherein the nozzle, sliver, insulation, liner and potting compound are composed of ablative-insulative materials. These ablative components comprise between 20 to 40 percent of the inert weight of the missile.

Rocket motors are constructed of composite materials, with each component material performing a specific function depending on its location. This type of construction is optimum, since the environmental conditions and hence the required materials properties vary greatly with motor position. Figure 16 illustrates this point by presenting the relative magnitude of gas temperature, velocity, pressure and their associated effect on surface heating and shear in various sections of an advanced solid propellant motor. In the aft end of the motor, an internal insulative material is used to protect the external structural case. It serves to transmit the chamber pressure forces into the wall, and insulate the external structural element from the high temperatures and reactive products of the combustion gases. The insulator should be flexible to permit it to follow (without cracking) the case expansion during motor ignition. A low modulus material is required to prevent high stresses in the liner-case bonded areas.

In general, motor insulators are composed of modified phenolic or epoxy impregnated asbestos materials. Recently, very promising results have been obtained with silica filled elastomers and epoxy modified polyurethanes. Environmental conditions become more severe in the entrance cone of the nozzle, and associated materials requirements change significantly. Increased material rigidity, structural strength, and thermal insulation are required. Some degree of dimensional surface change is permitted, since its influence on thrust is small. Refractories (metals, ceramics and graphites) are generally unsuitable for the entrance section of an uncooled nozzle, because of the size and configuration involved, and associated materials properties. Instead, fiber reinforced plastics which form a surface char, and possibly a viscous melt during heating, appear to be optimum. They consist usually of a phenolic-asbestos, phenolic-graphite fiber, or oriented silica fiber reinforced phenolic composition. The most critical part of the nozzle is the throat section, which experiences the highest level of heat flux (up to about 2,000 Btu/ft²-sec), gas shear, and particle erosion. The original configuration and dimensions of the throat must remain constant throughout motor firing to insure non-variant chamber pressure and thrust conditions.

Ablative materials are seldom used in the nozzle throat, except for low chamber pressure motors or very short duration firings. Better performance is generally obtained with a refractory insert of tungsten, metallic carbide, high density graphite or pyrolytic graphite. These materials suffer from thermal shock failure, low elongation, and high thermal conductivity. This latter property requires the use of an insulative backup in the throat region. Material requirements for this insulator section are: high thermal stability, little or no gasification at temperature, high strength, moderate to high modulus, high heat capacity and moderate thermal conductivity. High temperature resins (phenolics, phenyl silanes and silicones) containing vitreous or asbestos fibers are often used in this region.

As the exhaust gases pass into the exit cone, the temperature and pressure levels decrease and the velocity increases. Added problems of high gas turbulence, shock wave effects, and acoustic vibrations impose structural stresses and possibly asymmetric ablation. Exit cone materials should be very light because of the large size involved, and they should ablate uniformly at a minimum rate for optimum nozzle efficiency and thrust vector control. The materials of construction are generally oriented (shingle- or end-grain) silica or carbon fabric reinforced plastic. In some cases, a random oriented quartz, or silica fiber plastic molding are used. The external structural elements of the rocket supports the mechanical and thermally induced stress, which are due to internal gas pressure, vibration, acceleration, thrust vector control and differential thermal expansion of component materials. To accommodate these factors, the structural material should have high strength, adequate modulus, and resistance to buckling. Either a high temperature metal (steel, titanium, aluminum) or a glass filament wound plastic are generally suitable for the nozzle exterior.

The use of ablative nonmetallic materials in liquid-fueled motors has been equally impressive, but certainly not as extensive. The factors which tend to limit the use of ablators in liquid-fueled rockets are: frequent lack of need for uncooled parts since the fuel may serve as its own coolant, burning times are relatively long, and engines are often proof tested by static firing.

One of the most impressive developments in the application of ablative materials to liquid propulsion systems is the ablative skirt for the second stage engine of the Titan ICBM. This hybrid nozzle is shown in figure 17. It is composed of a small regenerative cooled nozzle and a larger, uncooled extension. The purpose of the ablative skirt is to achieve optimum thrust at high altitudes, allow for a "dry jacket" altitude start thus minimizing pre-launch preparations, and preclude the possibility of engine compartment contamination by fuel leakage during first stage missile operation. The uncooled ablative skirt is constructed of an asbestos reinforced phenolic liner stiffened with a glass fabric reinforced phenolic honeycomb.

Ablative materials have been used successfully for uncooled, low thrust chambers of space control rockets. In these liquid propellant motors, the fuel flow is too low to provide regenerative cooling; some other form of cooling is required. Surprisingly, certain ablative reinforced plastics have exhibited remarkable durability during firing exposures on the order of 22 minutes. Furthermore, they have performed successfully with several thousand successive restarts of the engine. An exploded view of this type of rocket motor is shown in figure 18. The forward combustion chamber is composed of a phenolic resin reinforced with an oriented leached glass fabric, followed by a silicon carbide throat, and then an exit cone of a phenolic resin containing randomly oriented leached glass fibers. After assembly of the motor parts, the structure is filament wound with glass filaments and epoxy resin.

Future Challenges

The combined efforts of the materials researcher, fabricator, evaluation engineer and designer have resulted in the creation of a variety of ablative materials and their successful application to hyper-environments. Because of the unique aspects of future environments and the ever constant design trend towards increasing materials requirements,

these materials may exhibit poor performance or be entirely unusable. Serious consideration must therefore be given to the forthcoming hyperthermal environments in an effort to:

- a. Determine the potential of existing ablative materials for more severe heating conditions.
- b. Identify critical and unusual aspects of future environments, and determine the balance of materials properties and characteristics required to accommodate these conditions.
- c. Provide basic guidelines for future research on ablative materials.
- d. Assure the availability of new and improved ablative materials for advanced designs as they are conceived.

Atmospheric Entry Environments

The trend toward longer ranges and higher entry speeds of ballistic missile nose cones is resulting in significantly higher aerodynamic heating rates and applied mechanical forces. The higher peak heating rates do not present unsolvable problems because the thermal efficiency of most ablators increases with the severity of the thermal environment. However, high dynamic pressures may cause crushing and premature failure of a mechanically weak ablating surface. Higher gas shear stresses accelerate the mechanical erosion of a solid or molten ablating surface. For example, melting ablators may experience greater sloughing than vaporizing of the surface molten material. These environmental factors could mean catastrophic failure or at least greatly reduced thermal efficiency of many ablative materials. New techniques for structural reinforcement of ablative materials are obviously needed.

Ballistic entry satellites and other related vehicles encounter a relatively long period of heating at moderate incident fluxes during hypersonic atmospheric entry. Aerodynamic forces acting on the vehicle are comparatively low, and for this reason, the structural aspects of the ablative material may be de-emphasized to achieve maximum insulative capability. Low temperature ablators ($< 1000^{\circ}\text{F}$) are required, and they may possibly be synthesized by building "thermally weak chemical bonds" into the molecular structure. Low density ablators are required for this heating environment which have a thermal conductivity of $0.025 \text{ Btu-ft/hr-}^{\circ}\text{F}$ or lower.

The radiative flux encountered by present vehicles during entry into the earth's atmosphere constitutes only a small fraction of the total heating rate. However, higher velocities at lower flight altitudes will present an increasingly serious problem of radiative heating. Energy predominantly in the ultraviolet to near infrared spectra will be radiated from the hot air boundary layer to the vehicle surface. Similarly, hypersonic flight into other planetary atmospheres such as Venus and Mars will likely involve high radiative heating. This combination of radiative-convective heating presents new thermal protective problems, since the gaseous species leaving the ablating surface are largely radiation transparent. The most promising technique for accommodating combined radiative-convective heating is high surface re-radiation, coupled with a small amount of mass transfer from the ablating material. The formation of an emissive, refractory surface material during ablation is very desirable, since optimum surface radiation occurs at maximum values of temperature and emittance.

Ablative materials will likely be used for thermal protection of future aerospace vehicles as they enter hypersonically into other planetary atmospheres. In the time interval between vehicle launch and planetary entry, an ablative material will be exposed to the elements of the space environment. It will be necessary, therefore, to determine the resistance of candidate ablative materials to wide temperature variations, high vacuum, meteoric impact, and solar, cosmic, and Van Allen radiations. Individual and synergistic influences of the space environment have yet to be determined. Entry into planetary atmospheres of different chemical and physical compositions will introduce new problems, and both theoretical and experimental investigations will have to be made on the behavior of ablative materials behavior in simulated planetary atmospheres.

A superorbital vehicle when entering a planetary atmosphere at escape velocities will produce a very high energy shock wave ahead of itself. Theoretical studies have indicated that high enthalpy environments are best accommodated by material vaporization and subsequent mass transfer in the boundary layer. New light-weight ablative materials which gasify completely into very low molecular weight products should exhibit considerable promise.

Superorbital vehicles may encounter multiple heating phases during atmospheric entry, thus requiring a re-start capability for the ablative material. For example, some initial ablative heat protection may be required for a vehicle decelerating in the upper edges of a planet's atmosphere. The vehicle may then be maintained in a predetermined park orbit in preparation to planetary landing. Meanwhile, the external ablative material must aid in thermal control of the vehicle. Subsequently, the remainder of the ablative material is expended as the vehicle is commanded to land. Synthesis of new ablators and the tailoring of these for this complex environment will indeed present formidable challenges.

Entry vehicles of the future will probably be provided with some degree of lift for vehicle stability and control. The aerodynamic fins may be subjected to extremely high environmental temperatures, which will require some form of thermal protection. Present ablative materials may not be satisfactory in this type of application since high dimensional changes may occur in the region where the gas stream is redirected. New ablators with very high dimensional stability will be necessary.

Rocket Propulsion Environments

Remarkable advances in rocket propulsion technology have been achieved. For the future, we can expect to see many new design concepts and continued improvements in the performance, reliability, and versatility of rocket propulsion systems. These developments will create a host of new material problems, since currently available materials will likely be unable to accommodate the new environmental parameters. Trends in design and associated environments are listed in figure 19, and the material requirements generated by them are discussed below.

Higher Temperatures—The continued development of higher performance propellants will, in certain cases, lead to appreciably higher combustion flame temperatures. At present, the temperature level is about 5400°F for a typical aluminized polyurethane propellant. Recent solid-fuel developments have extended this value to about 6300°F, with indications of continued increases up to 7000°F and higher. This trend in combustion temperatures is causing greater thermal shock, thermal stresses, and surface heating of ablative propulsion materials. At the highest flame temperatures, refractory throat materials will no longer be usable due to melting or excessive sublimation. It may be necessary to increase material vaporization upstream to the throat to provide some degree of film cooling to this critical area of a rocket nozzle.

Reactive Combustive Species—Improvements in rocket propellants and oxidizers is resulting in combustion products with greater chemical reactivity, corrosiveness and oxidation potential. Interaction of these combustion products with the ablating wall materials will likely result in greater material vaporization, because of deleterious exothermic reactions. Ablative materials will be needed which form a chemically inert surface during exposure to rocket exhaust products.

Surface Abrasion—Energetic particles of aluminum, lithium, beryllium, and boron may be used in future propellants to increase combustion stability and specific impulse. Impact of these particles on the ablating wall will lead to mechanical attrition of varying magnitudes. New ablative materials and novel techniques for handling the severe impact and shear of entrained liquid and solid particles are thus required.

Greater Thermal Shock—Future airborne operations at high altitudes and tactical missions may involve environmental temperatures down to about -75°F. Protection of the missile with special heating equipment is not desired, based on considerations of added weight, increased complexity, and lowered reliability. The ablative propulsion materials will therefore be conditioned at very low temperatures prior to motor firing. This will lead to two new problems, namely, increased thermal shock of the wall materials during initial motor firing, and possible cracking of the case insulation due to its inability to yield with motor pressurization. Ablative materials are required with better thermal shock resistance and low temperature properties.

Longer Burning Times—Two current developments in solid propellant technology will likely result in a considerable increase in firing duration from the present values of 30 to 70 seconds. These are the advent of the segmented motor, and the trend toward very large solid propellant motors. Ablative materials with useful service lives on the order of 100 seconds and longer will be required.

Higher Chamber Pressures—The chamber pressures of current solid propellant motors range from 100 to 2,000 psia, with the majority of values between 400 and 700 psia. The mean chamber pressure of solid-fueled rockets will tend to increase slowly in the future, and possible plateau at a value of about 1,000 psia. Increasing problems of material surface are expected, as well as increased structural requirements for the ablative materials.

Non-Uniform Erosion—The flow of combustion gases may be diverted in certain areas of a propulsion system to achieve proper motor design or thrust vector control. For these cases, non-uniform elliptical erosion may occur in the areas where the gas stream is diverted in direction. Materials and design techniques are required for maintaining better dimensional stability in these critical areas.

Ablators for New Designs—Many new designs in rocket propulsion systems are presently being evolved, and consideration should be given to the possible application of ablative materials to these systems.

Solid propellant motors of very high thrust are being designed either as a large unsegmented engine or as smaller segmented (building-block) motors. Multi-million pound thrust motors having diameters up to 14 feet, lengths up to about 63 feet, and burning times on the order of 85 seconds are being studied. The segmented motor approach involves multiple staging of conical propellant charges, which may be fired sequentially for optimum thrust. Each motor segment or group of segments are fitted with an uncooled ablative nozzle. The large number of possible motor thrust ratings and engine

designs requires a far greater understanding of ablative materials for use in this wide spectrum of rocket exhaust environments.

As flame temperatures and corrosivity increase from their present level, attention is being focused on new nozzle configurations. One of the most promising developments is the application of plug-type nozzles to uncooled solid engines. This nozzle is of a mushroom shape design, and provides maximum exhaust expansion for minimum nozzle length and weight. It is competitive with the clustering of four DeLaval nozzles typically used on large solid propellant motors. A major limitation of the plug nozzle is the large mass of material which must be contained in the region of highest heat flux. Consequently, the amount of coolant required could be large to prevent excessive wall temperatures. The applicability of ablative materials to plug nozzle design is as yet relatively unexplored, and further work is required to define the materials problems involved.

Another interesting approach towards reducing the nozzle length and weight is the "internal" nozzle. This design concept is simply a conventional nozzle which has been recessed into a conventional or spherical motor case. Since both sides of the nozzle walls are exposed to the hot combustion gases, requirements for cooling are increased considerably.

Consumable rocket motor cases for solid propellants is another appealing concept for weight saving. In this application, the propellant charge is surrounded by an ablative material which is consumed as the fuel is advanced through the nozzle section. The selection of ablative materials and associated problems are currently on the study stage.

Some attention too is being focused on hybrid rocket motors which offer promise for volume-limited missile systems, thrust modulation, and on-off control of upper stage rockets. Work has been conducted with various hypergolic propellant combinations and liquid oxidizer systems. Ablative material problem areas are largely undefined, and thus some consideration should be given to this motor design.

To achieve variations in thrust and burning rates, new propellant grain designs are being investigated. The internal burning chamber designs of new motors (such as the spherical rocket engine) utilizes a propellant web to protect the fore and aft closure during burning. Less insulative material is thus required for thermal protection of the motor wall. On the contrary, the slotted tube configuration permits the combustive gases to erode the exposed motor wall sections, since the flame contacts these areas throughout firing. The requirement for an effective insulating liner for these new grain designs is apparent.

The use of composite materials in rocket propulsion systems is increasing rapidly. Problems encountered in fabrication and joining are more difficult, due to the dissimilar materials properties. Each basic material component reacts in a characteristic way to the hot propulsion environment, which leads to difficulties in maintaining them as a single functional element. New knowledge and techniques are required for fabricating advanced rocket engine components of various materials having greatly dissimilar thermophysical properties.

Finally, each new rocket design has a multitude of miscellaneous heating problems which may involve the use of ablative thermal barriers. Some of these problems are: skin heating of solid fueled rockets as they exit from the earth's atmosphere, combustion gases seeping back into the booster compartment of the missile, radiant heating due to the clustering of rocket engines, silo and ground equipment heating, and similar considerations.

Summary

The significance of ablative materials to aerospace technology is now apparent. Our successes in solving the re-entry heating problem and in providing light-weight, high performance propulsion materials are history. The current state of the art represents only first generation developments, and only a small portion of the hyper-environmental spectrum has been investigated. Current material deficiencies must be overcome, and new ablative materials with unique properties and characteristics are necessary. Each new success in this work will permit a wider range of aerospace systems and new capabilities in aerospace technology.

BIBLIOGRAPHY

- WADC TR 57-638 "Effects of High Intensity Thermal Radiation on Structural Plastic Laminates", H. Schwartz and B. Lisle, December 1957.
- WADC TR 59-87 "Determination of Factors Governing Selection and Application of Materials for Ablation Cooling of Hypervelocity Vehicles", J. Bonin, C. Price and D. Taylor, July 1959.
- Ibid, Part II, July 1959.
- Ibid, Part III, J. Bonin, C. Price and H. Halle, February 1960.
- WADC TN 59-251 "Degradation Effects of High Intensity Thermal Radiation on Plastic Radome Materials", R. Farmer, July 1960.
- WADC TR 59-366 "Thermal Protection of Structural, Propulsion, and Temperature Sensitive Materials for Hypersonic and Space Flight", J. Bonin and C. Price, May 1960.
- Ibid, W. Manos, D. Taylor and A. Tuzzolino, July 1960.
- WADC TR 59-368 "The Study of Ablation of Structural Plastic Materials", F. Vassallo, N. Wahl, G. Sterbutzel and J. Beal, December 1959.
- Ibid, Part II, April 1960.
- WADC TR 59-459 "Effects of High Temperature, High Velocity Gases on Plastic Materials", F. Baltakis, D. Hurd and R. Holmes, June 1960.
- WADC TR 59-574 "Behavior of Plastic Materials in Hyperthermal Environments", D. Schmidt, April 1960.
- WADC TR 59-656 "Determination of Properties of Sandwich Materials Subjected to Rapid Rising Temperatures Summary Technical Report", C. Haudenchild, July 1960.

BIBLIOGRAPHY (Cont'd)

- WADC TR 59-668 "A Study of the Mechanism of Ablation of Reinforced Plastics", R. Mixer and C. Marynowski, February 1960.
- Ibid, Part II, D. Chamberlain, Jr., D. Van Sickle and C. Marynowski, February 1961.
- WADD TN 60-88 "Analysis of Relative Performance of Ablating Materials Compared to a Heat Sink Material", R. Otto, June 1960.
- WADD TR 60-90 "Thermal Parameters of Re-Entry Ablative Plastics", D. Schmidt, March 1960.
- WADD TR 60-101 "Conference on Behavior of Plastics in Advanced Flight Vehicle Environments", H. Schwartz, September 1960.
- WADD TR 60-109 "Development and Evaluation of Solid Propellant Rocket Motor Case Insulating Materials Systems", J. Batchelor, N. Vasileff, S. McCormick and E. Olcott, June 1960.
- Ibid, Part II, May 1961.
- WADD TR 60-110 "Thermal Protective Surfaces for Structural Plastics", J. Vogan, July 1960.
- Ibid, Part II, October 1960.
- WADD TR 60-193 "Thermal Erosion of Ablative Materials", D. Robbins and G. Epstein, February 1960.
- WADD TN 60-286 "Properties of Thermally Degraded Ablative Plastics", H. Schwartz, D. Schmidt, S. Marolo and D. Starks, November 1960.
- WADD TR 60-314 "The Thermal Diffusivity of a Structural Plastic Laminate at Elevated Temperatures", R. Farmer, September 1960.
- WADD TR 60-359 "Experimental Studies to Determine the Chemical Species Prevalent in the Plasma of an Air Arc and the Boundary Layers Adjacent to Ablating Materials", R. Carrigan, E. Raisen and K. Schmude, August 1960.
- WADD TR 60-380 "Reinforced Plastics at Very High Temperatures", D. Schmidt, and George Peterson, June 1960.
- WADD TR 60-439 "Metal-Ceramic Ablative Coatings", R. Eschenbach and R. Wickham, January 1961.
- WADD TR 60-507 "Heat Protective Ablative Coatings for Radomes", J. Cavanaugh and J. Sterry, August 1960.

BIBLIOGRAPHY (Cont'd)

- WADD TR 60-646 "Carbonization of Plastics and Refractory Materials Research", J. Coffman, G. Kibler, T. Riethof, and A. Watts, February 1961.
- WADD TR 60-647 "Thermal Irradiation of Plastic Materials", H. Schwartz and R. Farmer, 1961.
- WADD TR 60-648 "Ablative Behavior of Plastics in Subsonic and Supersonic Hyperthermal Flow", R. Farmer, November 1960.
- WADD TR 60-649 "Comparative Erosion Resistance of Plastic Materials in a Supersonic Rocket Exhaust and Subsonic Air Arc Plasma", H. Schwartz, September 1960.
- WADD TR 60-697 "Study of Thermal Radiation Within Solids and Study of Internally Ablating Composites", F. Vassallo, H. Kirchner, G. Sterbutzel and J. Beal, 1961.
- Ibid, Part II, Volume I, May 1961.
- WADD TR 60-856 "Microstructure of Ablative Plastic Chars", S. Marolo, February 1961.
- WADD TR 60-862 "Ablative Plastics for Re-Entry Thermal Protection", D. Schmidt, January 1961.
- WADD TR 60-926 "Evaluation of Material Systems for Use in Extreme Temperature Environments Utilizing an Arc Plasma Jet", J. Rosenbery, H. Smith and J. Wurst, March 1961.
- WADD TN 61-48 "Ablative Thermal Protection for Aerospace Vehicles", D. Schmidt, March 1961.

ACKNOWLEDGEMENTS

The author acknowledges with appreciation the use of the following photographs:

Figures 7 and 9	Bendix Corporation
Figure 8	General Electric Company - M.S.V.D.
Figures 10, 11, and 17	Aerojet-General Corporation
Figure 12	Atlantic Research Corporation
Figure 13	The Martin Company
Figure 14	The B. F. Goodrich Company
Figure 15	McDonnell Aircraft Corporation
Figure 18	North American Aviation - Rocketdyne

Type of Facility	Gas Enthalpy (Btu/lb)	Gas Velocity (fps)	Gas Mass Flow (lb/sec)	Stagnation Point Conditions		Test Fluid Composition	Available Testing Time (min)	Test Area Diameter (ft)	Principal Advantages	Principal Disadvantages
				Pressure (psf)	Initial Heat Flux (Btu/ft ² -sec)					
Chemical Torch (oxy-acetylene)	1,000	100 to 750	0.002 to 0.021	50 to 1,000	100 to 650	Combustion products	Near continuous	0.04 to 0.14	Inexpensive. Simple and rapid materials screening device.	Low enthalpy. Small exposure area. Chemical reactivity of gases.
Rocket Motor (oxy-gasoline)	1,500 to 3,500	7,000 to 8,000	0.5	10,000 to 80,000	300 to 3,000	Combustion products	0.5 to 10	0.08 to 0.70	Simulates actual rocket exhaust environment. Accommodates large model sizes. High stagnation pressures and supersonic flow.	Inability to change heat flux without greatly affecting stagnation pressure.
Electric Arc Heater (500 kw)	1,000 to 20,000	1,500 to 2,500	0.005 to 0.040	2,000 to 4,000	100 to 1,500	Air, argon, nitrogen or helium in molecular, dissociated, and ionized states.	Near continuous	0.03 to 0.10	Means for continuously heating variety of gases to very high temperatures	Low mass flow. Small exposure area. 0.1 to 5% electrode contamination of gas. High power requirement.
Electric Air Arc Tunnel (500 kw)	2,500 to 12,500	2,000 to 15,000	0.005 to 0.040	200 to 2,000	100 to 1,500	Air in molecular, dissociated and ionized states.	Near continuous	0.03 to 0.15	Re-entry simulation.	Low mass flow. Small exposure area. 0.1 to 5% electrode contamination of gas. High power requirement.
Graphite-Resistor Furnace	1,300	3,000	0.03	6,000	200 to 800	Inert gases or air	0.1 to 3.0	0.04 to 0.10	Inexpensive. Versatile.	Erosion of furnace walls. Small exposure area.
Pebble Bed Heater	1,200	3,600 to 5,500	0.1 to 10	70 to 15,000	50 to 400	Air	0.1 to 2.5	0.04 to 0.08	High stagnation pressure.	Small exposure area. Air temperature declines (100F/sec) with exposure time. 0.5 to 1.0% ceramic dust contamination of gas.
Arc Image Furnace	--	0	0	0 to 2,000	50 to 2,500	Vacuum, or any gas	15 to 30	0.02 to 0.08	Non-contaminated heat source. Control of environmental conditions. Variety of available chemical environments.	No imposing aerodynamic flow. Highly absorbent surface required. Small exposure area. Surface volatiles interfere with radiant transmission.

Table 2

CROSS-SECTION (x20) of AN ABLATED GLASS FIBER REINFORCED PHENOLIC

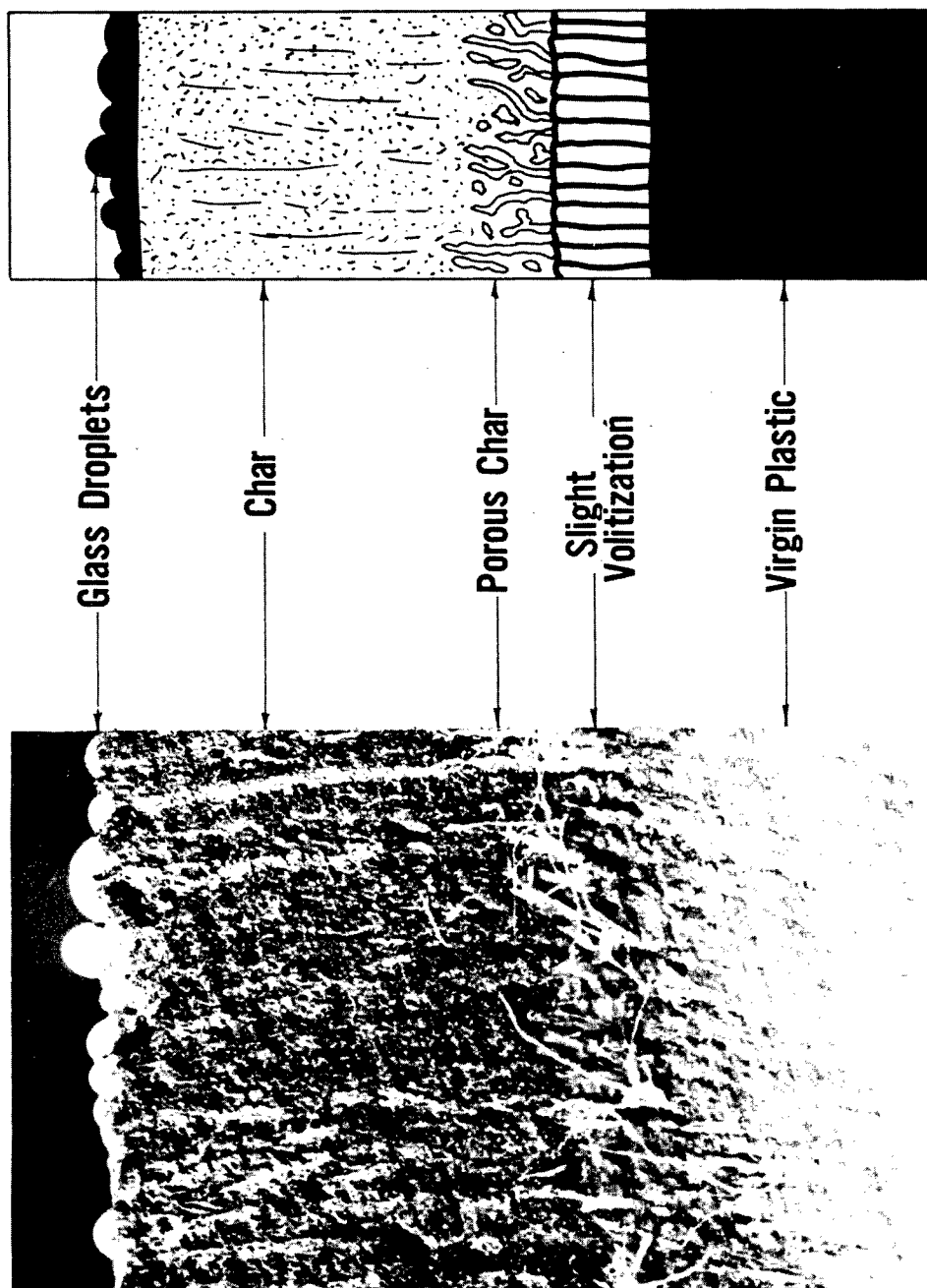


Figure 1.

THERMAL ACCOMMODATION PARAMETERS of ABLATION

Sensible Heat Absorption

Chemical Reactions

Phase Changes

Mass Transfer

Radiation

Figure 2.

ABLATIVE MATERIAL SYSTEMS

Advantages	Limitations
● High Heat Absorption And Dissipation	● Susceptible To High Mechanical Forces
● Exceptional Thermal Insulation	● Service Life Is Time Dependent
● No Maximum Service Temperature	
● Weight Savings	
● Resistance To Thermal And Mechanical Shock	
● Availability	
● Design Simplicity And Flexibility	
● Non-Strategic Materials	
● Low Cost	
● Passive In Operation	

Figure 3.

THE IDEAL ABLATIVE MATERIAL

Desired Trends			
-----> ∞	-----> 0	-----> 1	Variable
Heat Of Ablation	Thermal Conductivity	Surface Emittance	Ablative Temperature
Strength	Density	Fraction Vaporized	Melt Viscosity
Enthalpy Of Phase Changes	Dimensional Erosion		Melt Surface Tension
Specific Heat	Molecular Weight Of Volatiles		
Thermal Shock Resistance			

Figure 4.

ENVIRONMENT INFLUENCES ABLATIVE PERFORMANCE

Thermal	Mechanical	Chemical
Mode Of Heat Transfer	Pressure	
Total Heat Load	Shear	Reactivity
Shape Of Heat Pulse	Vibration	Oxidation
Peak Heating Rate	Acceleration	Reduction
Heating Time	Deceleration	

Figure 5.

RESEARCH ON ABLATIVE MATERIALS

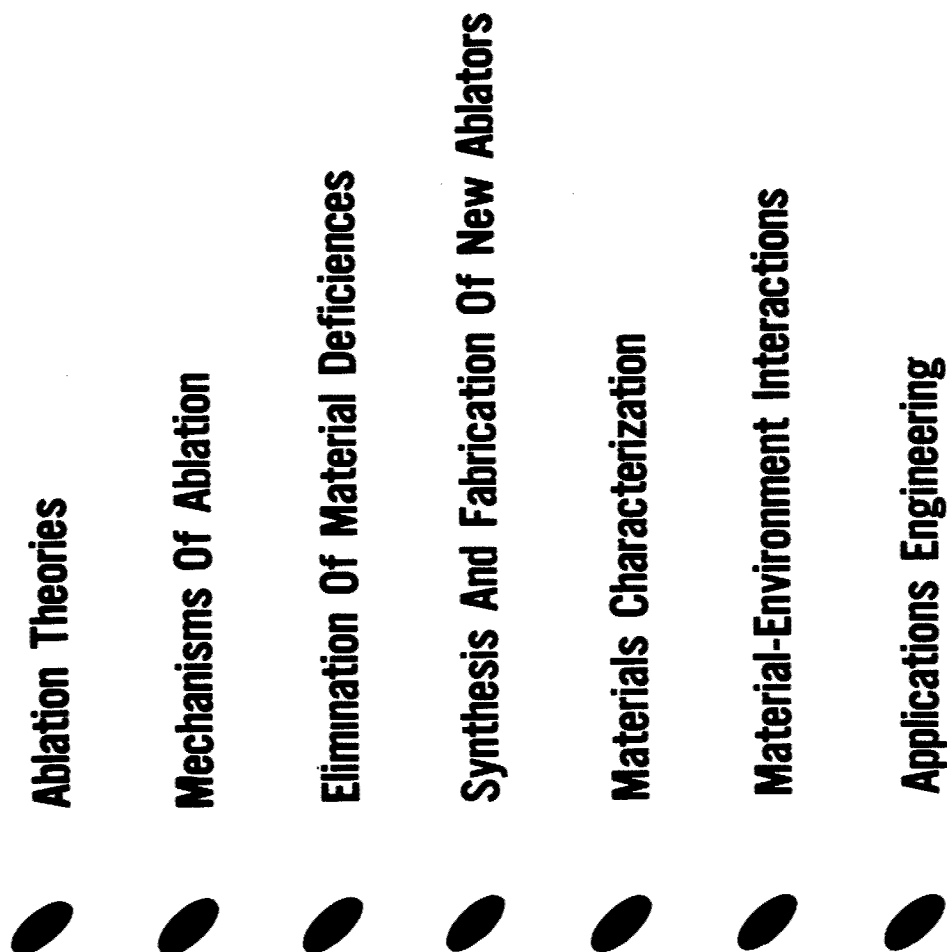


Figure 6.

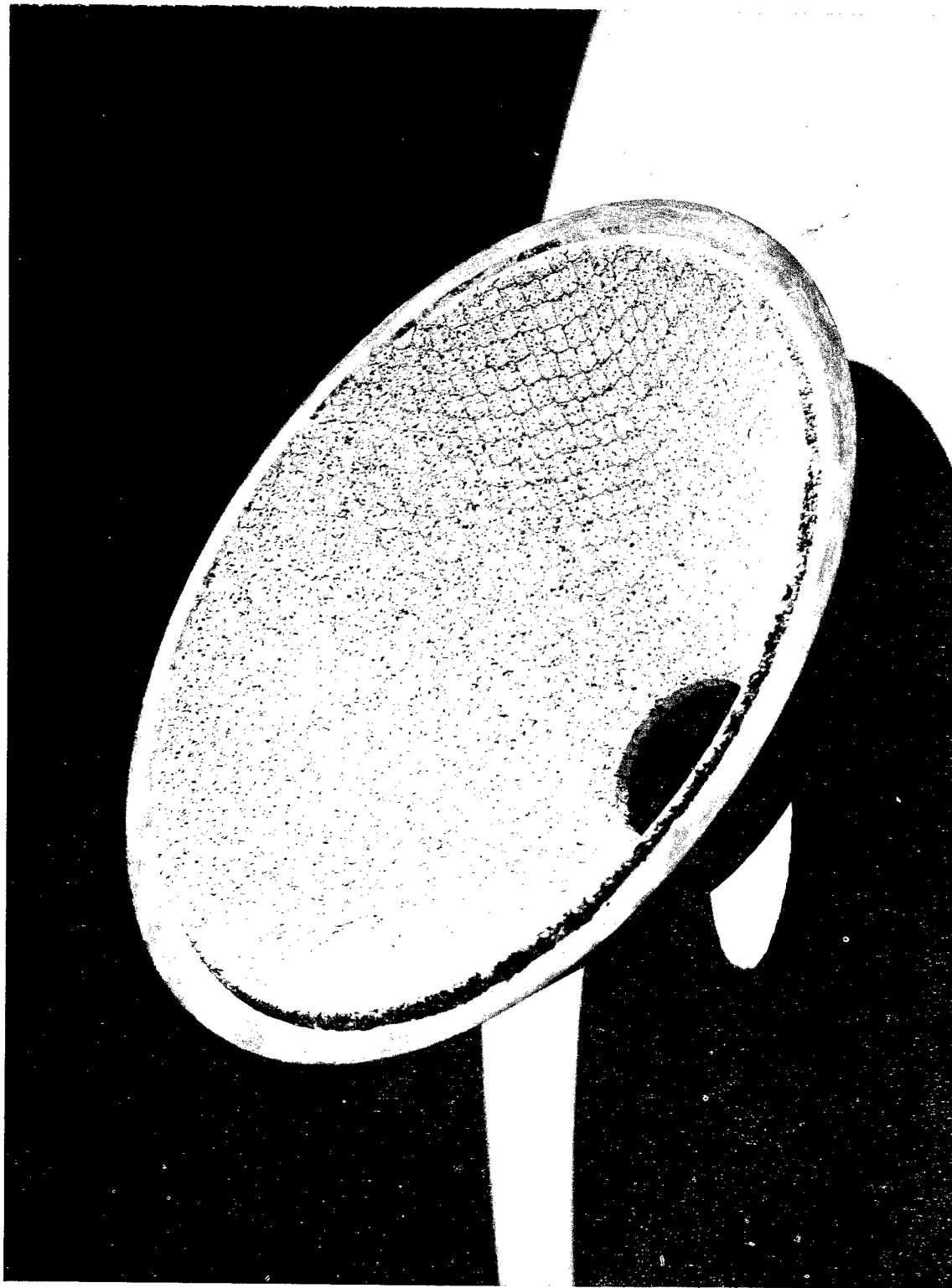


Figure 7. Composite Entrance Cone For Uncooled Rocket Nozzle

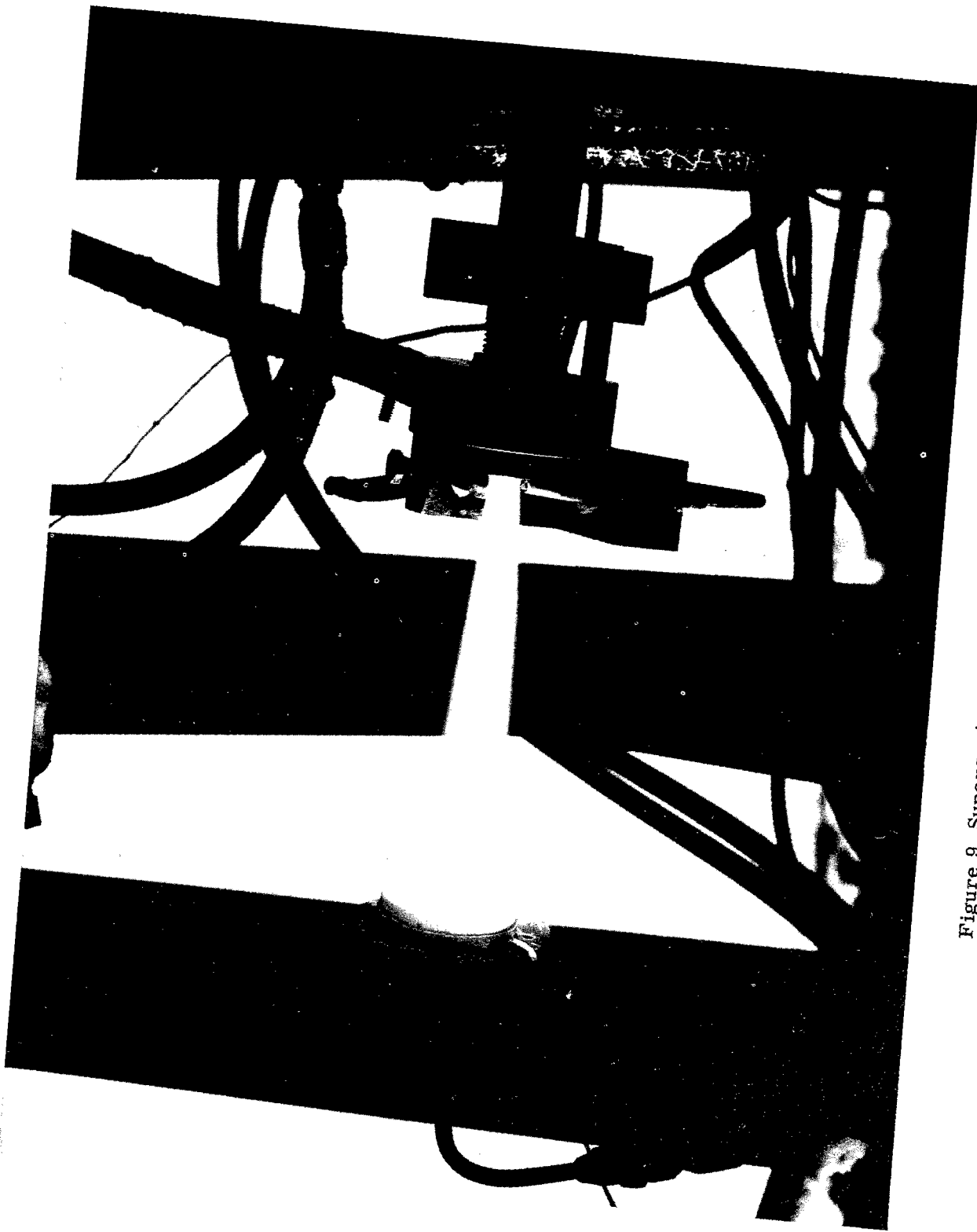


Figure 9. Supersonic Oxy-Acetylene Torch Facility

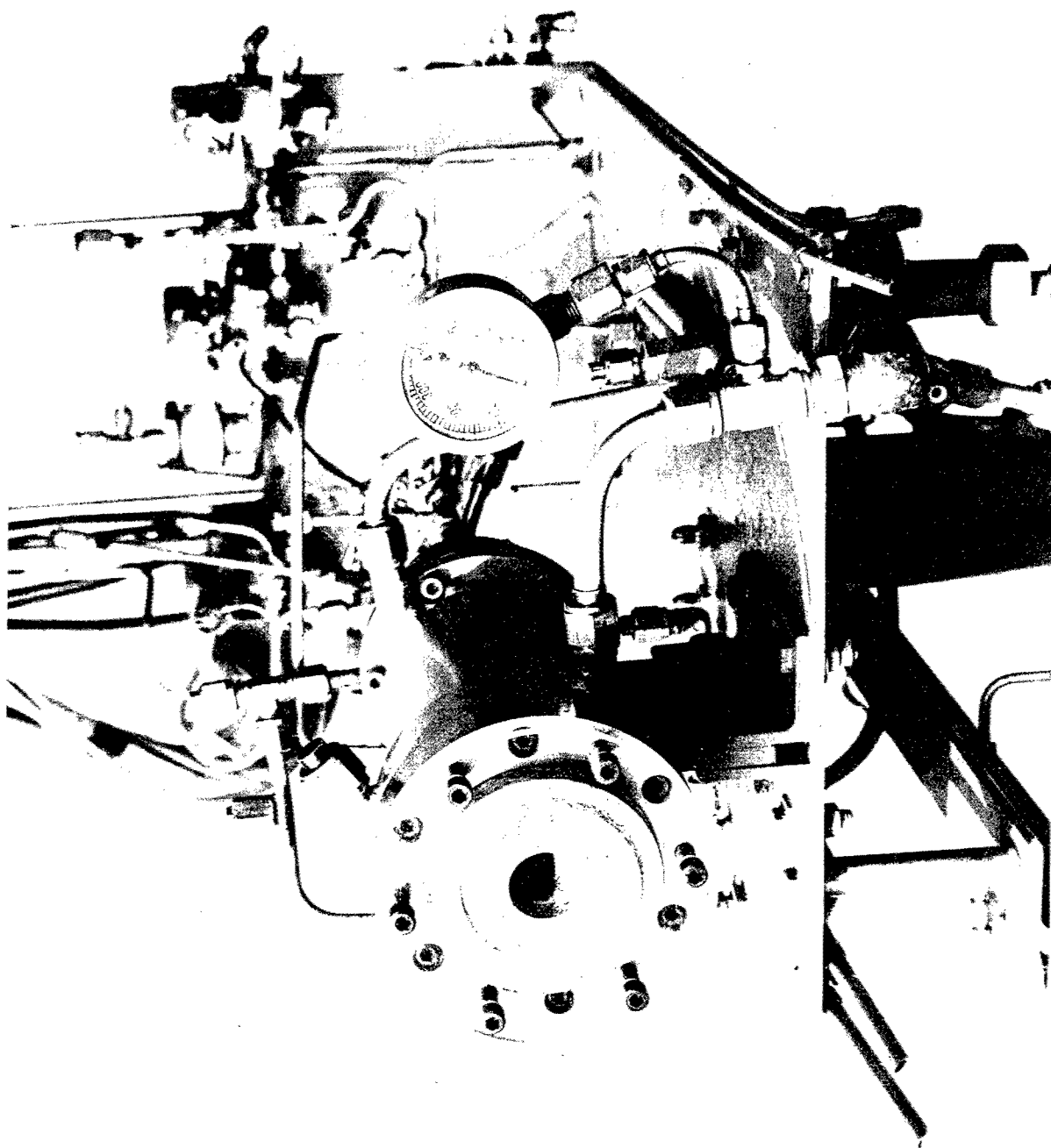


Figure 10. Gaseous Hydrogen-Oxygen Motor For Materials Characterization

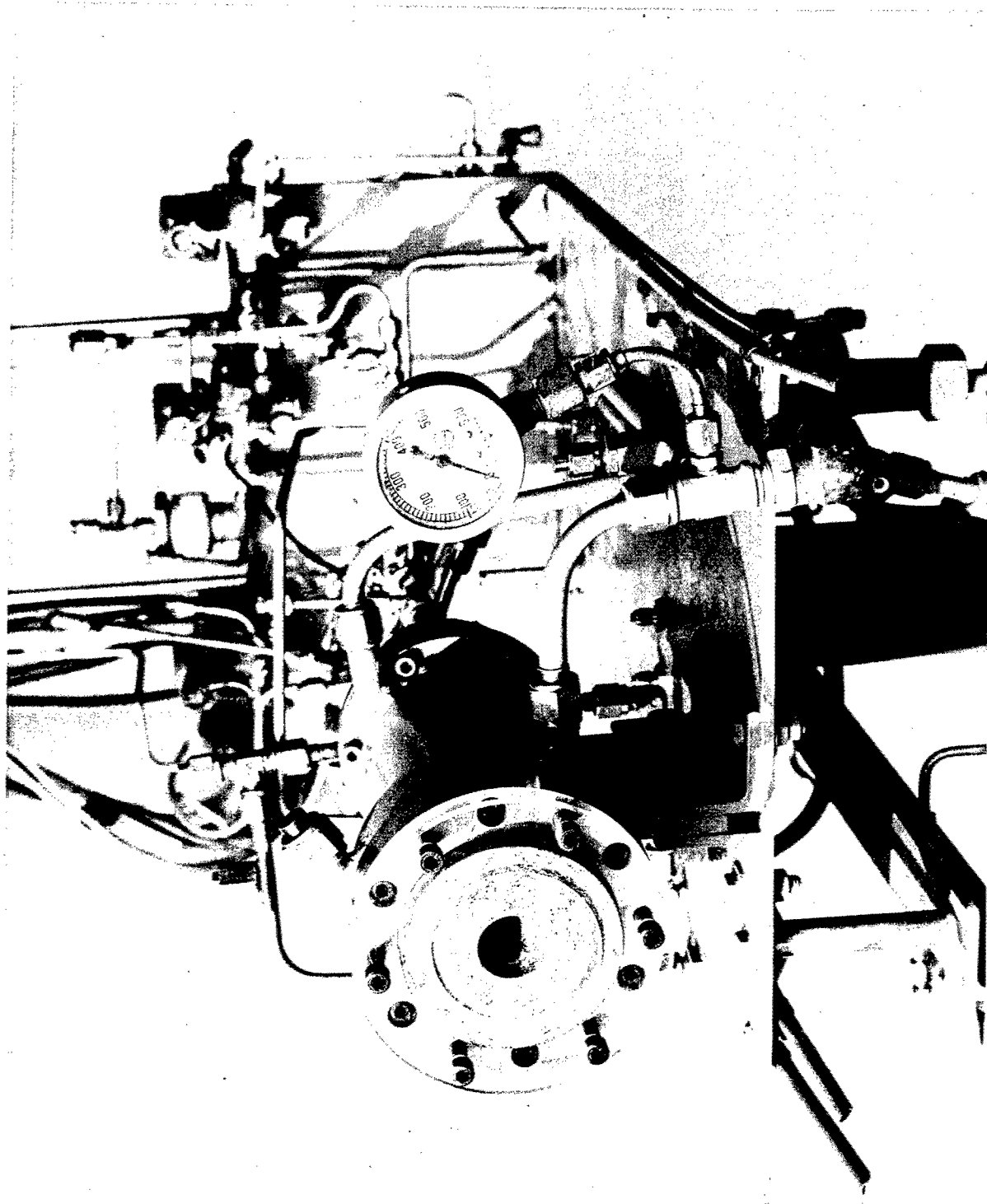


Figure 10. Gaseous Hydrogen-Oxygen Motor For Materials Characterization

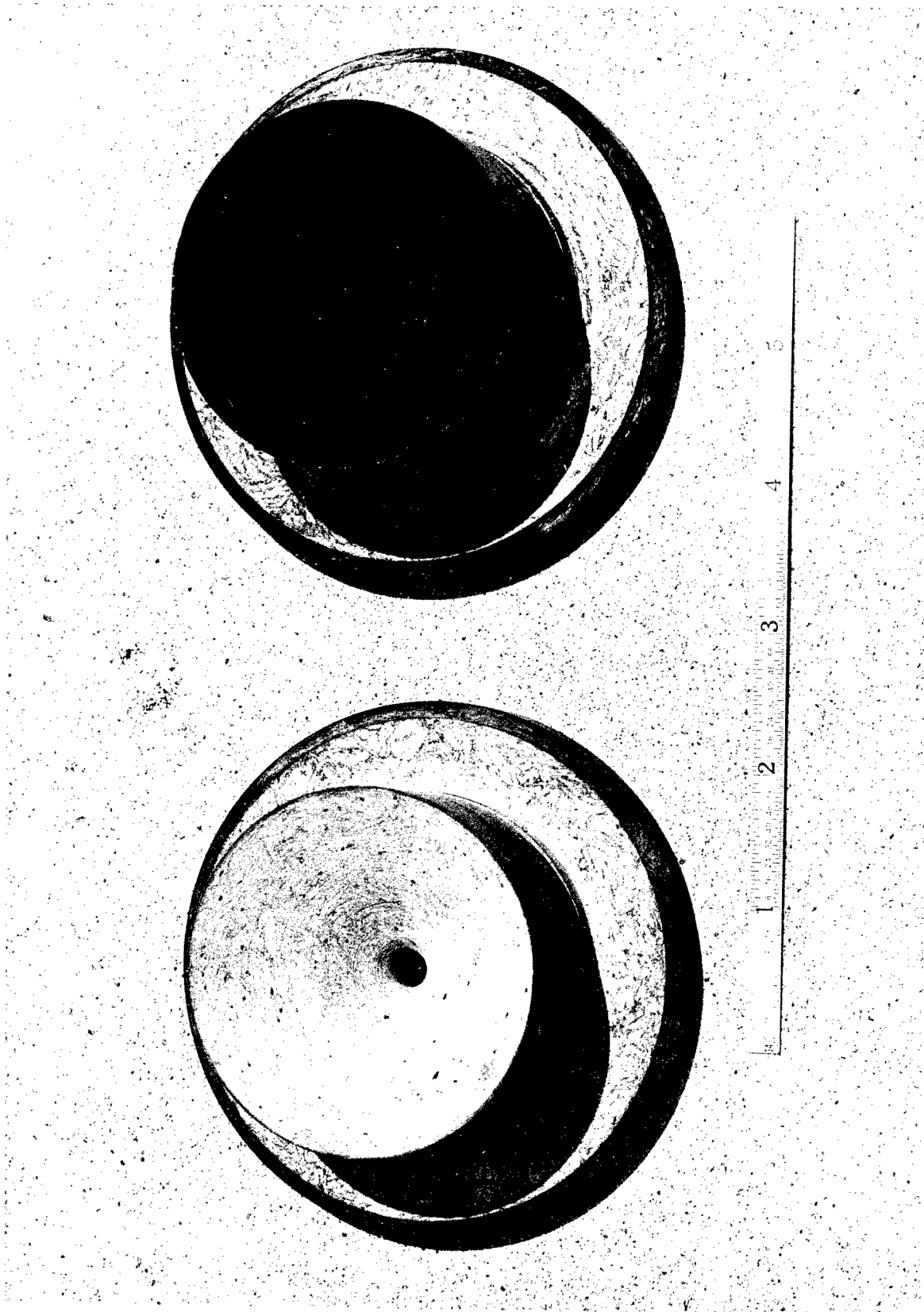


Figure 11. Research Nozzle Specimen Before and After Motor Firing

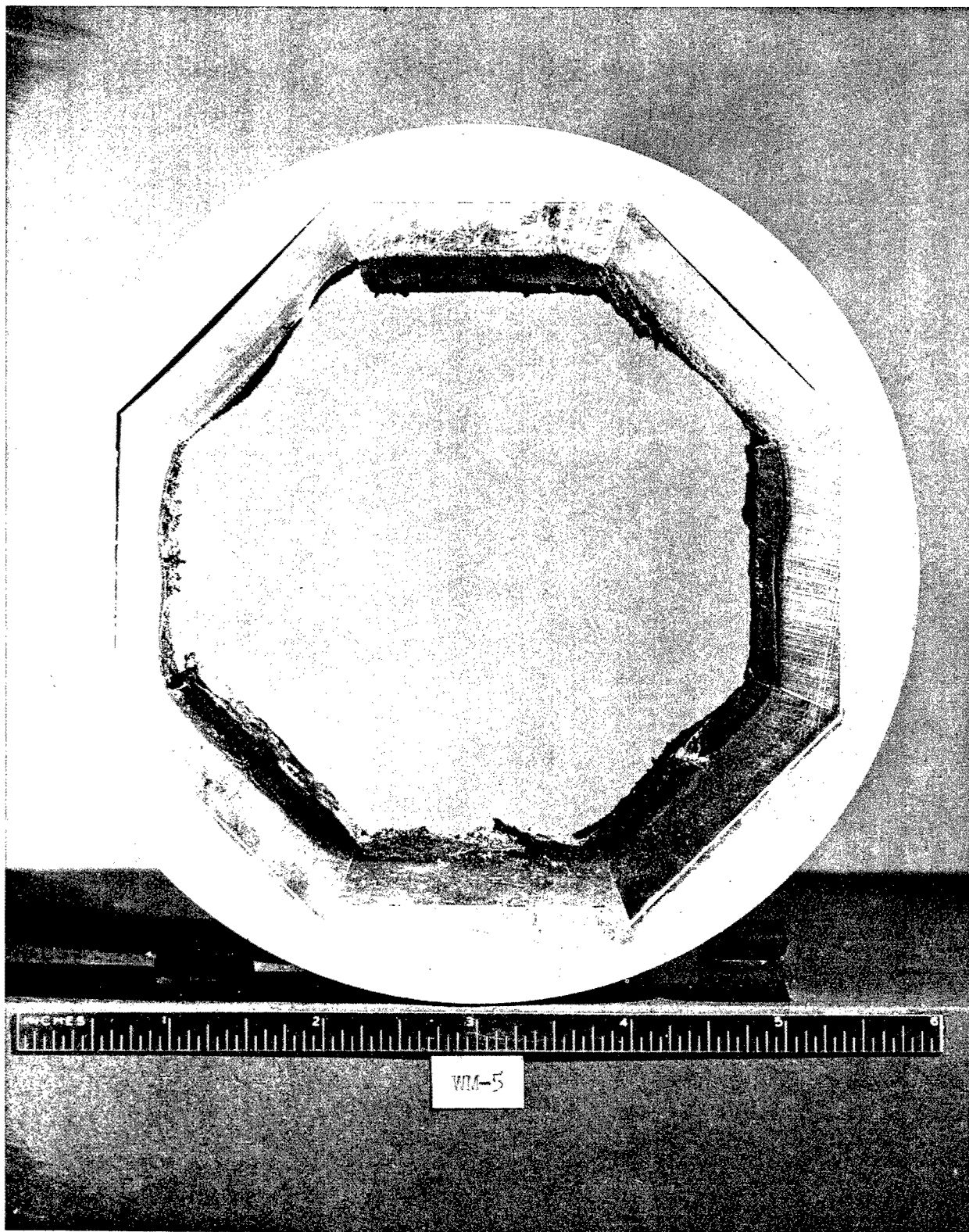


Figure 12. Ablative Insulators After Exposure to Solid Propellant Exhaust

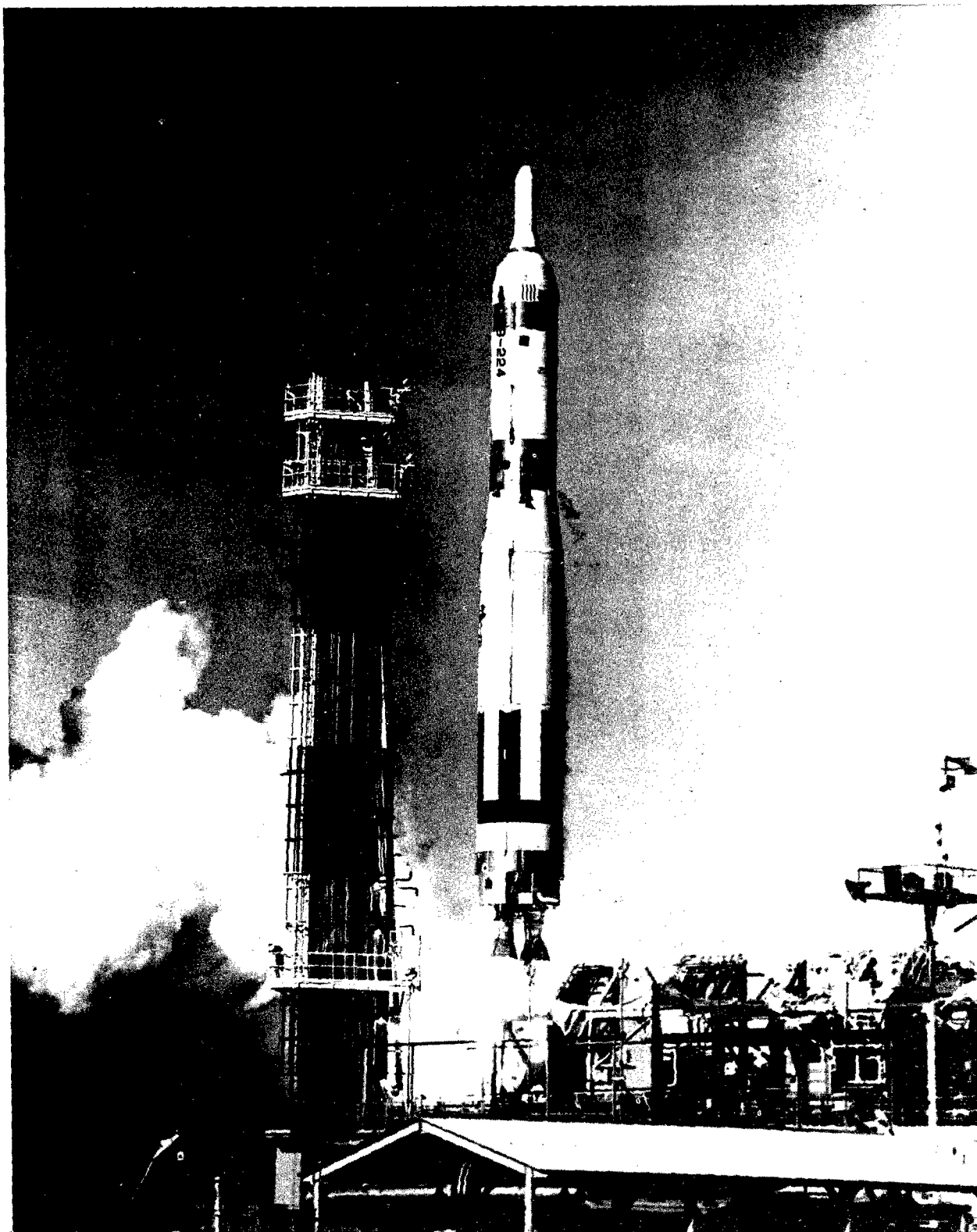


Figure 13. Ablative Materials Research Vehicle Being Launched by a Titan ICBM

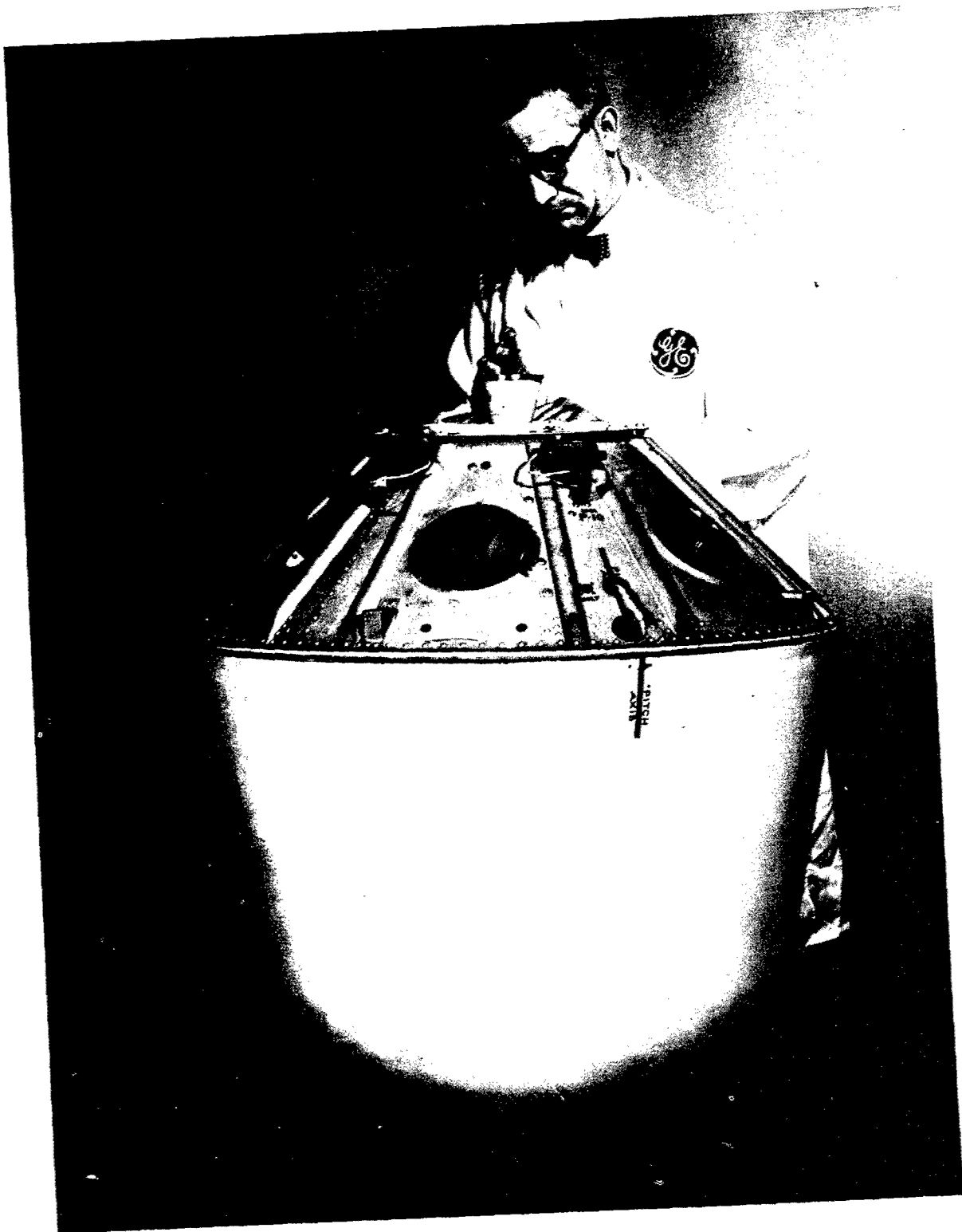


Figure 14. Discover Orbital Entry Capsule



Figure 15. Ablative Heat Shield on Manned Mercury Capsule

SCHEMATIC of AN ADVANCED SOLID PROPELLANT MOTOR

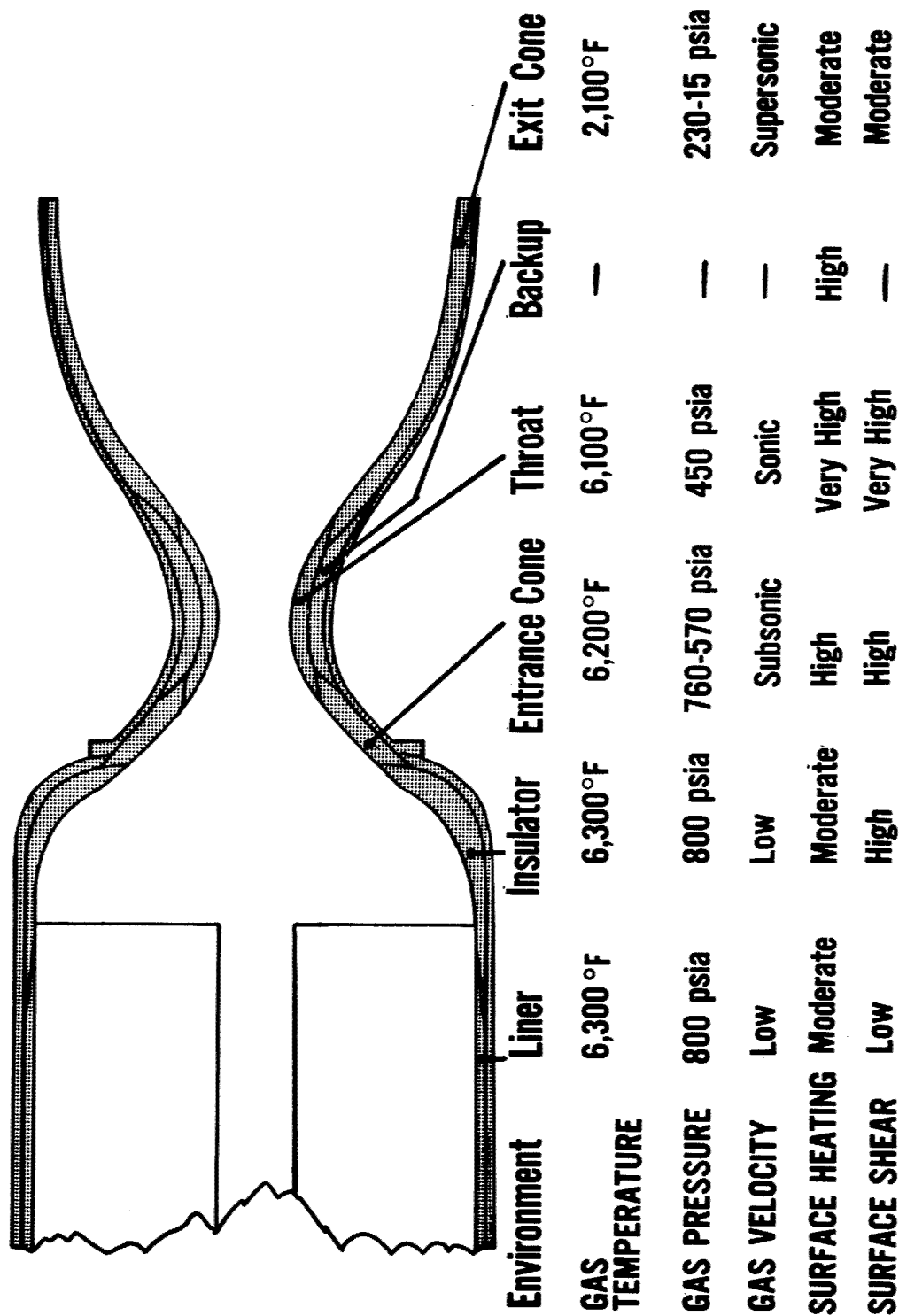


Figure 16. Schematic of an Advanced Solid Propellant Motor

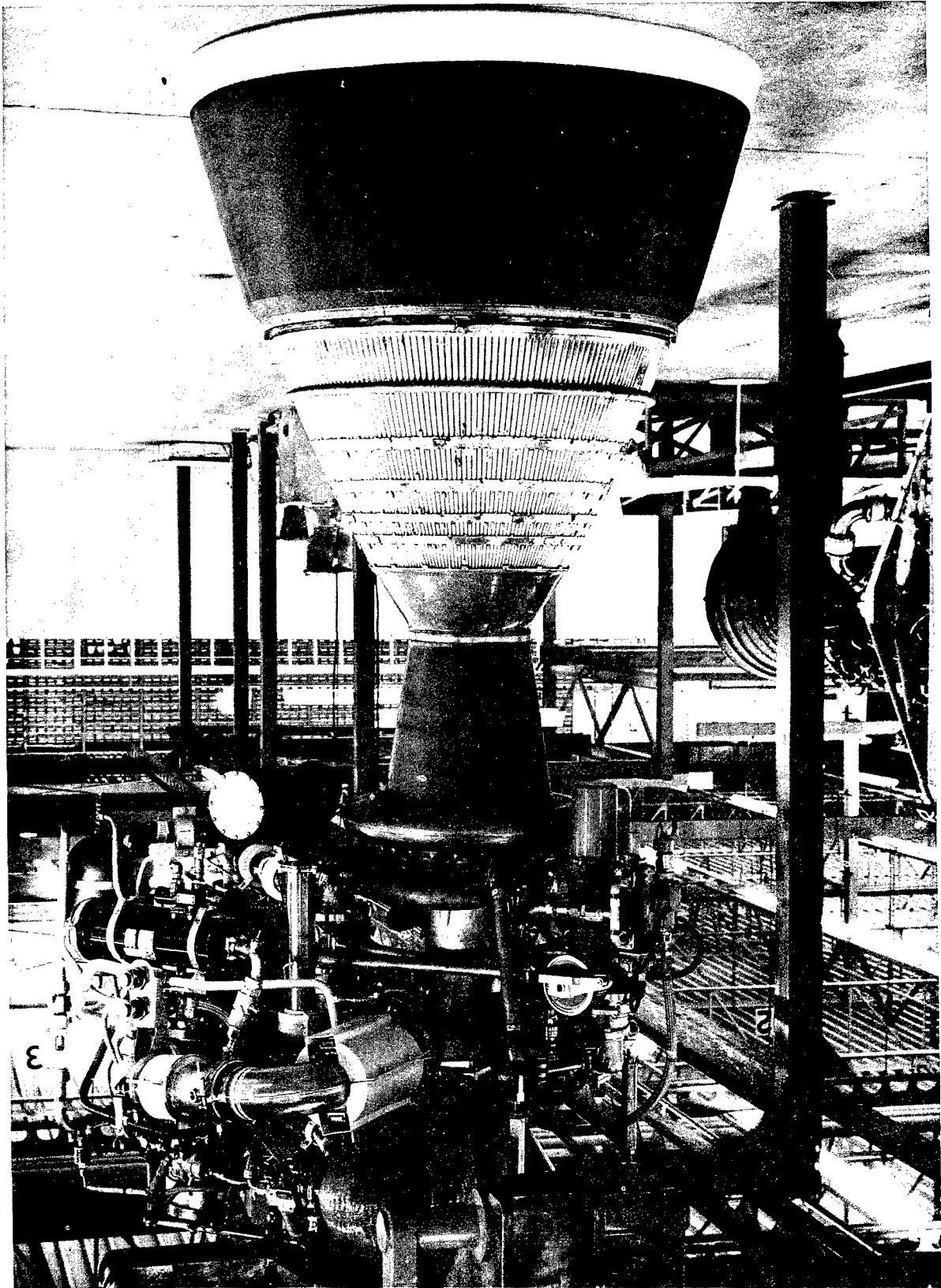


Figure 17. Ablative Skirt on Second Stage Titan Rocket Motor

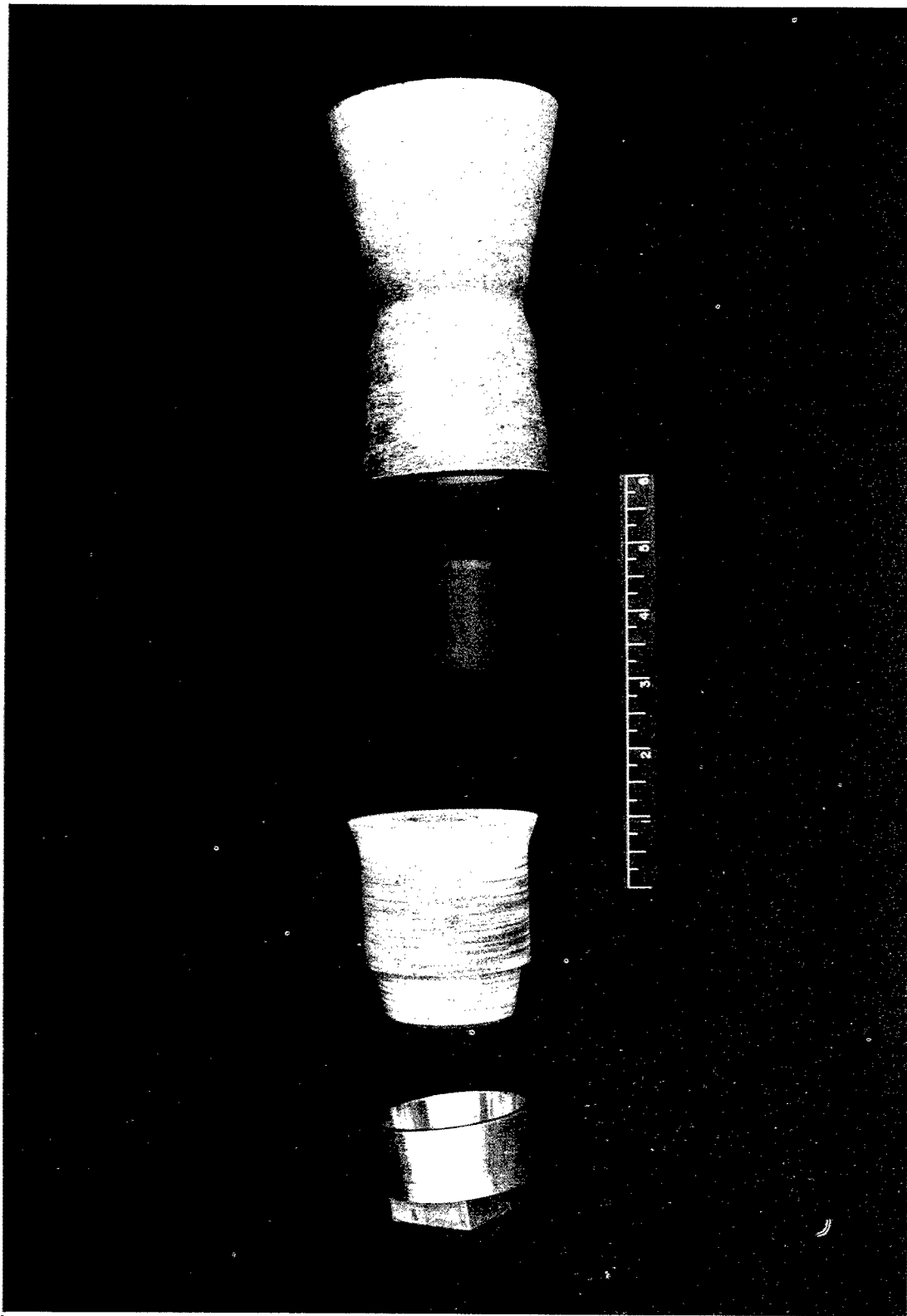


Figure 18. Exploded View of Uncooled Rocket Motor for Space Altitude Control

NEW TRENDS IN ROCKET PROPULSION SYSTEMS

Designs	Environments
High Thrust Boosters	Higher Temperatures
Hybrid Engines	Increased Chemical Corrosion
Re-Start Motors	Severe Particle Abrasion
Segmented Motors	Greater Thermal Shock
Thrust Vector Controls	Longer Burning Times
Nozzle Configurations	Higher Chamber Pressures
Unconventional Cases	Non-Uniform Gas Flow
Composite Construction	
Grain Configurations	

Figure 19. New Trends In Rocket Propulsion Systems

NEW TECHNIQUES FOR PROCESSING METALS

Chairman

Mr. C. W. Douglass

Speakers

Capt. P. S. Duletsky

Mr. J. Bryars

Panel Member

Mr. V. De Pierre

EXTRUSION OF HIGH TEMPERATURE MATERIALS

Paul S. Duletsky, Captain, USAF

Directorate of Materials and Processes, ASD

Introduction

The activity and technological advancement in the field of refractory metals, that is, molybdenum, tungsten, columbium, and tantalum, during the past two years is quite evident, even though the inherent problem areas of oxidation, protective coatings, joining, and room temperature brittleness are far from solution.

In the development of refractory alloys, like other base metal systems, the quality of the raw material, or ingot, is one of the major factors that control the effectiveness of the end product. The advancements in this area have been most pronounced. Conversely, commercial extrusion capability has not kept pace with alloy development nor the increased size and quality of refractory metal ingots.

Complete details of the current extrusion techniques and the metallurgical evaluation of the effects of extrusion variables on the secondary workability of the TZM alloy and the Mo-25W-.1Zr-.02C alloy will soon be published (5). This work will be reported by Harvey Aluminum, Incorporated, who operate and maintain the extrusion facility at the Directorate of Materials and Processes. In addition to accomplishing their own program with the TZM and the Mo-25W-.1Zr-alloy, Harvey Aluminum personnel have performed "service type" extrusion work for the Directorate of Materials and Processes alloy development program contractors and a variety of work sponsored by other governmental agencies.

When reference is made to the Directorate of Materials and Processes, it encompasses the specific program being conducted by Harvey Aluminum and work generated by the various co-operative programs listed in table 1.

Commercial Production Capability

As a general rule, high temperature materials denote high temperature processing, particularly with regard to the initial breakdown of the as-cast structure of refractory metals. Materials Advisory Board Reports of the Committee on Refractory Metals have consistently stressed the need to raise extrusion temperature capabilities. Until the recent installation of a 200 KW, 3000 cycle, induction heating station at the E.I. duPont deNemours extrusion facility (2) and a 60 cycle, 7500 KW, unit being installed at Curtiss-Wright (2), commercial production facilities were generally limited to a 2300°F-2600°F billet heating capability. There are, however, many reasons for this delay to increase billet heating capabilities. The most prevalent reasons being: (a) only glass lubrication appeared to be practical above 2400°F, which required a financial burden for license rights (b) specific quantity requirements could not be ascertained for a reasonable cost analysis of equipment modification amortization (c) the high volume materials, unalloyed molybdenum, and Mo-.5Ti could be satisfactorily extruded with conventional equipment, and (d) the die problem appeared formidable for extrusion above 2500°F.

Some of the earliest molybdenum extrusion work was performed by the Babcock and Wilcox Company, Tubular Products Division. A condensed "recap" of extrusion data,

pertaining to work performed during the period 1957-1959, is shown in table 2. Considering the fact that refractory metal extrusion was in its embryonic stage and make-shift material handling was utilized, a wide variety of alloys were successfully extruded. Most of these alloys were of an experimental nature and subsequently discarded; however, a great deal of knowledge was gained to advance the state of the art.

The Canton Drop Forge & Manufacturing Company has produced the greatest amount of refractory metal extrusions (1). Tons of unalloyed molybdenum and the Mo-.5Ti alloy have been extruded at Canton. Table 3 depicts the current capability with regard to billet size and extrusion ratio at 2300°F, the current temperature limitation. Although the 2300°F limitation dictated the extrusion of the "tougher" materials at lower extrusion ratios, this facility has served as the major producer of wrought refractory metals for several years. The successful extrusion of refractory metals into sheet bar was a highly desirable advantage for sheet rolling.

The new E. I. duPont deNemours extrusion facility has been in operation for a short time and the scope of the production capacity or specific refractory metals being extruded has not been determined. This facility certainly possesses a great potential in the extrusion of refractory metals as evidenced by the available information of the equipment already in operation (2,6):

- a. 2500 Ton, high speed (10 in/sec), extrusion press
- b. 200 KW, 3000 cycle, induction billet heater
- c. 4000°F maximum billet temperature
- d. 8.5" dia. x 24" long, maximum billet size

Work under the Columbium Extrusion Development Program sponsored by AF Contract 33(600)-40700 is being accomplished at this facility. Six ingots (7.75" dia. x 16-20" long) of the D-31 alloy (Cb-10Ti-10Mo) have been extruded at approximately a 5:1 ratio. The D-31 alloy has been extruded utilizing a .250-inch thick, mild steel can with very good results. It is anticipated that the final D-31 "T" shape will be extruded from a wrought billet. This facility is a Ugine-Sejournet licensee and details of lubrication are not available.

Pilot Plant and Research Laboratory Extrusion Facilities

The most significant advances in the high temperature extrusion (2500°F) of refractory metals has been accomplished in the pilot plant type facilities and/or research laboratories. The Allegheny Ludlum Steel Corporation (1,778 ton press) and the General Electric Research Laboratory (1,250 ton press) could be classified in a production category; however, insufficient detailed information regarding the production output is available. Most of the available literature of these two organizations pertains to extrusion work performed in container, liner sizes not greater than 4-inch I.D. and are considered as pilot plant type facilities in this presentation.

The Thompson Ramo Wooldridge Research Laboratory (700 ton high speed press) and the Directorate of Materials and Processes (700 ton high speed press), Aeronautical Systems Division, Wright-Patterson AFB, Ohio, are the two most active laboratory facilities engaged in the high temperature extrusion of refractory alloys. The Super Alloy Forge, Inc., Hamburg, Michigan, possesses mechanical presses of 1000 ton (horizontal)

and 400 ton (vertical) capacity (1). Some very interesting work in the extrusion of refractory metals has been accomplished by Super Alloy Forge and warrants a rather detailed discussion. This will be presented as a separate item of discussion later in the text.

Although differences do exist in equipment size, operational limitations, and techniques utilized, several aspects of general operation are shared in common. Relatively high ram speeds, conical dies, refractory coated dies, and glass lubrication are used to varying degrees by all five organizations. The most significant accomplishments or pronounced differences will be presented for each of the organizations:

The Allegheny Ludlum Steel Corporation

The Allegheny Ludlum Steel Corporation is a Ugine-Sejournet licensee and most of the published information regarding their work is derived from technical reports under government sponsored contracts. The following are considered to be the most significant results obtained in the Air Force "Molybdenum Alloy Extrusion Development Program" with the Mo-.5Ti-.08Zr-.02C alloy:

	<u>TEMP</u>	<u>RATIO</u>	<u>SHAPE</u>
ARC CAST	3740°F	11:4:1	ROD
WROUGHT	2900°F	17.25:1	ROD

A detailed report regarding the above work will be published soon (7).

The room temperature hardness of the wrought material was 206 DPH; billet length was 4.5 inches in a 3 7/8-inch container liner; a flat face die was used. The ability to extrude a "T" shape approaching commercial tolerances required for steel and titanium by utilizing wrought billets is certainly promising with this approach. The successful extrusion of some of the high strength refractory alloys currently being developed may require the adoption of this approach at considerably lower extrusion ratios.

General Electric Company Research Laboratory, Schenectady, New York

The General Electric Research Laboratory has been actively engaged in the hot extrusion of refractory metals, intermetallic compounds, and a variety of proprietary materials. The major portion of their work is of a semi-proprietary nature and consequently has not been published with any great amount of detail. Unalloyed arc-cast tungsten has been extruded at 3000°F and a 5.5:1 reduction (8). The F-48 alloy is being extruded on a production basis in molybdenum cans and a 4:1 extrusion ratio at 2800°F. They have also extruded a considerable amount of the TZC alloy (Mo-1.25Ti-.1Zr-.018C). General Electric has extruded the Mo-W series of alloys in conjunction with the Air Force alloy development programs with Climax Molybdenum. Glass lubrication and conical shaped dies are used. The extent to which ceramic coated dies are utilized is not known. The General Electric Research Laboratory is active in many areas of material development and a considerable amount of press time is absorbed by internal programs.

Thompson Ramo-Wooldridge, Inc. Research Laboratory

The Thompson Ramo-Wooldridge Research Laboratory has been a pioneer in the hot (3000°F) extrusion of refractory metals. The utilization of ceramic coated dies has led to the successful extrusion of the 85W-15Mo alloy with negligible die wash at 4000°F and extrusion ratios of 5:1-8:1. TRW is actively engaged in the "Tungsten Forging Development Program", Contract AF 33(600)-41629 (9,10). A considerable amount of experience in the extrusion of tungsten and tungsten alloys was derived through an extrusion program with NASA. Most of the initial columbium alloy extrusion development for duPont was done by the TRW Research Laboratory. This phase of work included a large number of alloys for experimental screening.

The TRW Research Laboratory has always differed significantly from other research extruders in that they have been the pioneers in utilizing higher temperatures, greater extrusion ratios, and higher ram speeds, that is 4000°F, 6:1-10:1, and ram speeds greater than 10 in/sec under load. Considerable die wash was experienced in this approach during the early work. New developments in refractory metal and/or ceramic die coatings have resulted in negligible die wash (.010"-.015") in the extrusion of the 85W-15Mo alloy at 4000°F and extrusion ratios of 6:1 to 8:1.

One of the novel techniques used by TRW is the utilization of the oxide formed on the surface of the billet as a lubricant, during the transfer from the heating station to the press. A current report (10) indicates that a lubrication study is contemplated.

The Super Alloy Forge, Inc., Hamburg, Michigan

An extremely interesting report (11) by E.J. Dulis and A. Kasak, Central Research Laboratory, Crucible Steel Company, includes detailed information on the extrusion of a tungsten, tantalum, molybdenum, and columbium series of new alloys. All of the extrusion work was performed by The Super Alloy Forge, Inc. The techniques used in the extrusion work are not only novel but indicative of the current trend in the approach to the solution of high temperature extrusion. The detailed description of the procedures and techniques utilized is highly commendable. A list of the alloys included in this work is shown in table 4.

The work was performed in a 400 ton vertical mechanical press with a six-inch ram stroke. Ram speeds at no load averaged 1200 in/min. The average size of the extrusion blanks was 1-inch O.D. x 1.5-inch long. Extrusion ratios ranged from 2.7:1 to 4:1, the majority at approximately 3:1. Carbon blocks were used as back-up material for most extrusions and Armco iron blocks were used for the most difficult materials to extrude.

The induction heater station was powered by a 100 KW, 9600 cycle unit with high pressure water cooling of the induction coil. The furnace tube was made of "KT" silicon carbide insulated from the induction coil by a .250-in. thickness of high temperature felt. Woven "Fiberglas" covered the induction coil and temperatures greater than 4000°F could be attained. An argon atmosphere was maintained in the heating chamber and billet temperatures were based on a time and power basis obtained by previous experimentation. Oxidation during heating was sufficient to eliminate optical pyrometer readings for each extrusion blank. The billets extruded at lower temperatures (2500°F and 3100°F) were precoated with a glass lubricant. Billets heated from 3500°F to 4000°F were plasma flame sprayed with a molybdenum coating from .010 inch to .015 inch thick.

Hardened hot-work steel dies (H-12) were used for extrusions up to 3100°F. A .010-inch thick layer of tungsten plus a .015-inch thick layer of molybdenum was plasma flame sprayed on dies for the higher temperature extrusions. The dies were designed with a 70 degree included entrance angle.

During the initial work, the transfer time* was 6 to 10 seconds. The cooling rate of the extrusion blanks at 4000°F was estimated to be 160°F/sec. In order to circumvent this temperature drop, an automatic device was constructed that reduced the transfer time to 1 to 2.5 seconds.

The tungsten and tungsten-tantalum rich alloys were the most difficult to extrude above 3500°F and were prone to transverse cracking. Although the as-cast hardness of the tungsten and tungsten-tantalum rich alloys ranged from 370 to 450 DPH, none of the extrusion blanks shattered under impact during the extrusion runs.

Directorate of Materials and Processes, ASD, Ohio

During the past two years, the development of new techniques for the extrusion of refractory metals has progressed from steel dies and grease lubrication, with optimum extrusion temperatures of 2400°F, to ZrO₂ coated dies and an all-glass lubrication with optimum extrusion temperatures of 3400°F to 3600°F. Two Mo-25W-.1Zr billets were extruded recently with a negligible die wash of .010 inch to .012 inch. The effectiveness of the glass lubrication at this temperature has not been determined, although surface conditions were comparable to some extrusions performed at lower temperatures. Front to back dimensions were within .010 inch to .015 inch.

The evolution of the extrusion techniques developed at the Directorate of Materials and Processes is described in detail in the progress and technical reports by Harvey Aluminum (5,12,13,14). Similar information is contained in the presentations being given at this technical conference and in a number of technical reports derived from refractory alloy development programs sponsored by the Air Force (15,16).

The operational capabilities and/or limits of the basic units of equipment and the glasses used for lubrication are shown in table 5. Flame sprayed Al₂O₃ coated dies are considered satisfactory up to 3400°F. Flame sprayed ZrO₂ coated dies have shown .010 inch to .015 inch die wash at 4100°F on two occasions and the temperature limitation has not been determined.

Molybdenum and Tungsten Base Alloys

More than 300 refractory metal billets have been extruded at the Directorate of Materials and Processes in the past two years. An effort has been made to determine a correlation of extrudibility to various properties of refractory metals, that is, hot hardness, recrystallization temperature, grain size, solid solution versus precipitation hardening type alloys, and others.

Analysis of available data has not substantiated any firm conclusion. This is not too surprising when one considers the many variables involved. The heterogeneous structure of the refractory metals and the many variables involved during the casting, conditioning, extruding, and even packing and shipping, tend to complicate the problems.

* Elapsed time between removal from furnace and completion of the pressure stroke.

Table 6 lists some of the alloys extruded at various temperatures and extrusion ratios with the best weight percentage recoveries obtained. This is a representative sample of the general results obtained.

It can be stated that molybdenum base alloys are relatively easy to extrude; in fact, reproducible high weight percentage recoveries have been established for all molybdenum alloys extruded. The tungsten base alloys have been extruded with lower weight percentage recoveries and more difficulty. The two 85W-15Mo extrusions, identified as stickers in table 6, were partial extrusions of less than 50 percent. The W-.1Zr-.01C alloy could hardly be moved at temperatures up to 3600°F at a 4:1 extrusion ratio. Almost all of these difficult-to-extrude billets fractured when ejected from the container liner, indicative of brittleness at high temperatures. The capability of the ZrO₂ coated dies to withstand temperatures above 4000°F will result in an improvement for tungsten extrusions. Some work has already been done at 3600°F and 3750°F, but the analysis was not completed in time for inclusion in this report.

Sintered Molybdenum and Tungsten

Table 7 lists the sintered molybdenum, tungsten, and 50Mo-50W billets extruded at various temperatures and extrusion ratios. The extrusion of the 70 percent dense, unalloyed molybdenum billets was unsuccessful, although some sound material was salvaged from the back end of the 6:1 extrusion. It may be possible successfully to extrude the low density, sintered molybdenum (70 percent) at higher temperatures, greater extrusion ratios, and with the utilization of relatively cold (1400°F) steel nose plugs.

There was a remarkable difference in extruding the high density molybdenum. The extrusion planning to these billets was based on arc-melted material. The extruded surfaces were excellent, with practically no evidence of nose burst. No internal defects were found. Although the 50Mo-50W extruded rod had a rough surface due to die wash, the extrusion was sound.

Both of the commercially pure tungsten billets had good surfaces. The 93.3 percent dense material had an internal, non-closure, approximately seven inches long from one edge to the other in the transverse plane. This non-closure was approximately .250 inch away from the center of the extrusion. It is difficult to determine whether the defect was due to the difference in density or to the small defects indicated during inspection. Ultrasonic inspection prior to extrusion indicated two slight defects but at approximately .750 inch from each end of the billet and approximately in the center of the billet.

The difference between the two W + 1% ThO₂ billets was quite evident. The difference in extrusion temperature and ratio was expected to have its effects; however, the front end of the 89 percent dense extrusion was torn severely and pieces from the extrusion were lying in the run out tube.

The extruded section of the W + 1% ThO₂ (97.5% dense) exhibited complete recrystallization at the outer edge of the rod to a depth of approximately .060 inch. Three sections of the extrusion were side flattened with height reductions of 68 percent, 82 percent, and 85 percent at 2600°F on a hydraulic forge press. No defects were observed at the 68 percent reduction and minor cracks at the leading edge were evident on the pieces with 82 percent and 85 percent reduction. The recrystallization temperature of the forged material was 3200°F. This material exhibited good surfaces throughout the processing cycle. Sound specimens of the 89 percent dense (W + 1% ThO₂) and the 93.3 percent dense (C.P.-W) were forged under the same conditions at a 50 percent reduction in height. Gross

cracking on all edges resulted. Additional work is being done and will include rolling of sound material. The workability of the high density (97.5%) W + 1% ThO₂ was quite pronounced.

REFERENCES

1. Santoli, P.A., "Molybdenum Alloy Extrusion Program," Allegheny Ludlum Steel Corporation. ASC* Interim Report 7-785(I), October 1960.
2. Dana, A.W., Jr., "Columbium Alloy Extrusion Program," E.I. duPont deNemours. ASC Interim Report #1 (Parts I and II), Contract AF 33(600)-40700, 30 June 1960.
3. "Tantalum Alloy Extrusion Program," Wah Chang Corporation. ASC Contract 33(600)-42369 (to be published soon).
4. "Tungsten Alloy Extrusion Program," Wah Chang Corporation. ASC Contract AF 33(600)-42395 (to be published soon).
5. Long, J.R., Tombaugh, R.W., and Green, R.C., "Development of Optimum Methods for the Primary Working of Refractory Metals," Harvey Aluminum, Inc. WADD Technical Report 60-418 Part II (to be published soon).
6. Dana, A.W., Jr., "Columbium Alloy Extrusion Program," E.I. duPont deNemours. ASC Technical Report 7-775(II), 16 February 1961.
7. Santoli, P.A., "Molybdenum Alloy Extrusion Program," Allegheny Ludlum Steel Corporation. ASC Interim Report 7-785 (II) (to be published soon).
8. Noesen, S.J., and Hughes, J.R., "Arc-Melting and Fabrication of Tungsten," Transactions of the AIME, Vol. 218, pp. 256-61, April 1960.
9. "Tungsten Forging Development Program," Thompson Ramo-Wooldridge. ASC Interim Report 7-797(I), 31 August 1960.
10. Lake, F.N., and Bresnyak, E.J., "Tungsten Forging Development Program," Thompson Ramo-Wooldridge. ASC Interim Report 7-797(III), March 1961.
11. Dulis, E.J., and Kasak, A., "Research on Workable Refractory Alloys of Tungsten, Tantalum, Molybdenum, and Columbium," Crucible Steel Company. WADD Technical Report 61-134, April 1961 (in preprint status).
12. Simonson, R.B., Long, J.R., Tombaugh, R.W., and Green, R.C., "Development of Optimum Methods for the Primary Working of Refractory Metals," Harvey Aluminum, Inc. WADD Technical Report 60-418, August 1960.

* Metallic Materials Branch, Manufacturing and Materials Technology Division, Wright-Patterson AFB, Ohio.

REFERENCES (Cont'd)

13. Tombaugh, R.W., and Green, R.C., "Development of Optimum Methods for the Primary Working of Refractory Metals," Harvey Aluminum, Inc., Progress Report No. 3, WADD Contract AF 33(616)-6377, October 1960.
14. Tombaugh, R.W., and Green, R.C., "Development of Optimum Methods for the Primary Working of Refractory Metals," Harvey Aluminum, Inc., Progress Report No. 4, WADD Contract AF 33(616)-6377, February 1961.
15. Semchyshen, M., and Barr, R.Q., "Extrusion and Mechanical Properties of Some Molybdenum and Tungsten Base Alloys," Climax Molybdenum Company, WADD Technical Report 61-193, March 1961.
16. Ogden, H.R., and Maykuth, D.J., "Scale-Up of Tantalum-Base Alloys," Battelle Memorial Institute, Second Quarterly Progress Report, Contract AF 33(616)-7452, 15 January 1961.
17. Toaz, M.W., Davies, G.F., and Johnson, R.D., "Production of Extrusion Billets of High Temperature Aircraft Alloys by Powder Metallurgy," Clevite Corporation, ASC TR 60-7-764, December 1960.

TABLE I
LIST OF VARIOUS EXTRUSION WORK PERFORMED AT THE DIRECTORATE
OF MATERIALS AND PROCESSES

<u>NASA — C.P.-W, canned in steel</u>	<u>Armour Research (Navy)</u> C.P.- Mo, 70 % dense
<u>G. E. Lamp Division (Navy)</u> Sintered billets of: Mo, W, W + 1% ThO ₂ , and 50 Mo - 50W, 4:1 - 8:1, 2100°F - 3400°F	<u>G. E., Evendale (AF)</u> TZC alloy, 7:1, 2900°F Mo - .5Ti, 7:1, 2700°F
<u>Naval Research Laboratory</u> Ti - 1.5V - 15Al, and Ti - 8Mn canned in mild and stainless steel	<u>Republic Aviation (AF)</u> 93 W - 7Mo, 5:1, 3400°F
<u>Kawecki Chemical Co. (AF)</u> C. P. Tantalum at 1800°F and room temperature	<u>Crucible Steel (AF)</u> F - 48, canned in Mo, Ti - 110AT, 316 stainless, and mild steel at 3000°F, 2600°F, and 2300°F and 4:1
<u>Clevite Corporation (AF)</u> Ph 15 - 7 Mo and Rene 41 unsintered, 70 % dense	<u>Universal Cyclops (AF)</u> C. P. - W at 3000°F, 4:1, bare and mild steel can
<u>National Research Corp. (Navy)</u> 90Ta - 10W, 85Ta - 15 W, 80Ta - 20W from 2500°F to 3150°F	<u>Climax Molybdenum (AF - Navy)</u> W - Mo series, and TZC alloy Mo - 1.5 Cb - .5Ti - .3Zr - .3C Mo - 1.5 Cb - .5Ti - .3C
<u>Westinghouse Electric (AF)</u> Cb - 1Ti - 1Zr - 5Hf Canned in steel at 1800°F	<u>Bendix (AF)</u> Cerametalix 2400 - 30 (Cr base + MgO, 90% dense), 6:1, 8:1, 10:1, and 12:1, and 2000°F and 2200°F
<u>Manufacturing Laboratories (AF)</u> C.P. - Mo - C.P. - W, 2500°F - 3200°F	

() - Sponsoring Government Agency

TABLE 2

THE BABCOCK AND WILSON COMPANY EXTRUSION DATA ON COMMERCIAL PURE
MOLYBDENUM AND MOLYBDENUM ALLOYS

MATERIAL	BILLET DIAMETER	REDUCTION RATIO	BILLET TEMP (°F)	EXT. PEAK	PRESSURE AVERAGE	EXT. RATE (I. P. S.)
C.P. - Mo	6.5	3.71/1	2460	1970	1600	—
C.P. - Mo	6.5	3.24/1	2540	1300	—	10.4
C.P. - Mo	7.0	3.74/1	2420	1650	1550	8.0 - 10.4
Mo + 1.25% V	6.970	2.91/1	2540 (est)	1820	1520	3.0
Mo + .7% V	6.5	3.24/1	2540	1970	1680	—
Mo + .7% V	6.5	2.84/1	2620	1500	—	10.8
Mo + .2% Zr	6.97	2.84/1	2550 (est)	2030	2030	—
Mo + .5% Ti	6.97	2.84/1	2550 (est)	1620	1530	—
Mo + 1.25% Ti	6.97	2.91/1	2550 (est)	1830	1640	2.6
Mo + 2.0% Ti	6.97	2.84/1	2550 (est)	1800	1600	—
Mo + .1% Co	6.97	2.91/1	2550 (est)	1520	1400	3.2
Mo + .6% Al	6.97	3.29/1	2550 (est)	1120	1120	3.6
Mo + 1.25% Cb	6.97	2.84/1	2550 (est)	1790	1680	—
Mo + 2% W + .04% Cr	6.97	2.84/1	2580	1380	1260	—

(Glass lubrication utilized for this work.)

TABLE 3
THE CANTON DROP FORGE & MFG. COMPANY EXTRUSION DATA

ALLOYS	RATIO TEMP(°F)	RAM SPEED	PRESSURE (Tons/in ²)	LUBRICANT	DIE MATERIAL	REMARKS
Toughest W alloy 85 W-15 Mo	2.8:1 2300	200 in/min	65	Fiske #604	H-12	Comparatively good surfaces. Very little nose cracking. Ultimate wt. % recovery not known
Largest W Billet Unalloyed W 5 5/8" dia.	4:1 2300	200 in/min	51	Fiske #604	H-12	
Toughest Mo alloy 50 Mo-50 W	4:1 2300	200 in/min	37	Fiske #604	H-12	Cracked practically full length.
Largest Mo Billet Unalloyed Mo 16" dia.	3:1 2300	150 in/min	30	Fiske #604	H-12	Good as extruded surface. Ultimate wt. % recovery not known.
Toughest Cb alloy 80 Cb-10 Ti-10 Mo	4.5:1 2300	150 in/min	50-60	Fiske #604	H-12	Good as extruded surface. Tail end cropping only. Ultimate wt. % recovery not known
Largest Cb Billet Cb-1% Zr 14 3/8" dia.	3.16:1 2300	150 in/min	30	Fiske #604	H-12	

1.9" x 5.5", 2.5 x 8", 3.1" x 8", and 3.5" x 8", and 3.75" x 8" sheet-bars have been extruded from 7 1/2", 9", and 11" diameter ingots of unalloyed molybdenum, Mo-.5Ti, and Cb-1% Zr. Maximum ratio was 5.9:1. Lubrication, ram speeds, and die materials were as shown above. Temperatures were 2200°F and 2300°F and pressures did not exceed 58 Tons / in²

TABLE 4
REFRACTORY ALLOY COMPOSITIONS IN CURRENT
DIRECTORATE OF MATERIAL AND PROCESSES ALLOY DEVELOPMENT PROGRAMS

Battelle Memorial Institute		Crucible Steel Company			
Contract AF 33 (616)-7452		Contract AF 33 (616)-6172			
		<u>W</u>	<u>Ta</u>	<u>Mo</u>	<u>Cb</u>
Ta-10Hf-5W		100	—	—	—
Ta-30Cb-7.5V		75.3	24.7	—	—
		50.4	49.6	—	—
		25.3	74.7	—	—
Battelle Memorial Institute		—	100	—	—
Contract AF 33 (616)-5888		88.8	—	—	11.2
Ta-30Cb-5V		68.2	20.6	—	11.2
Ta-30Cb-10V		44.2	44.4	—	11.2
Ta-1Zr		20.7	68.1	—	11.2
Ta-10V		—	88.6	—	11.4
Ta-10V-5W		88.4	—	11.6	—
Ta-10Hf-1Zr		68.0	20.4	11.6	—
Ta-10Hf-5Mo		44.2	44.2	11.6	—
Ta-30Ti-5Al		20.4	67.9	11.7	—
Ta-40Ti-5Al		—	88.3	11.7	—
Ta-40Ti-10Al		88.6	—	5.7	5.7
Ta-30Ti-5Al-5Cr		68.1	20.5	5.7	5.7
		44.3	44.3	5.7	5.7
		20.6	68.0	5.7	5.7
		—	88.6	5.7	5.7
Westinghouse Electric Corp.					
Contract AF 33 (616)-6933					
W-2ThO ₂	W-.5ZrC				
W-4ThO ₂	W-.5CbC				
W-5ThO ₂	W-.5HfO ₂				
W-1TaC	W-.2TiO ₂				
W-2WB	W-.15TiC				
W-.5B ₄ C	W-1.0ZrO ₂				
Westinghouse Electric Corp.					
Contract AF 33 (616)-6258					
Cb-5Ti	Cb-2.5Cr	Cb-10Re	Cb-5V-5Mo-1Zr		
Cb-7.5Ti	Cb-5Mo	Cb-18Re	Cb-5W-5V		
Cb-20Ti	Cb-10Mo	Cb-.6Al	Cb-5W-5V		
Cb-10Zr	Cb-20Mo	Cb-1.5Al	Cb-5W-5V-1Zr		
Cb-20Zr	Cb-10W	Cb-2.5Al	Cb-5Hf-5V		
Cb-10Hf	Cb-20W	Cb-1Y	Cb-5Zr-5V		
Cb-1.25Cr	Cb-2Re	Cb-5V-5Mo	Cb-5W-5Hf-5V		

TABLE 4 (Cont'd)

Climax Molybdenum Company
Contract AF 33 (616)- 7930

Mo-1.5Cb-.5Ti-.3Zr-.05C
 Mo-2Ti-.3Zr-(.07C, .14C, and .21C)
 Mo-3Ti-.5Zr-.3C
 Mo-25W-1.25Ti-.3Zr-.15C
 Mo-50W-1.25Ti-.3Zr-.15C
 Mo-25W-1.25Ti-.3Zr-1.5Cb (.05C, .1C, and .15C)
 Mo-50W-1.5Cb-1.25Ti-.3Zr-.15C
 W-(.01-.03Zr)-.01C
 W-5Ta - Zr to be
 W-5Cb - determined
 W-5Cb-5Ta-

Climax Molybdenum Company
Contract AF 33 (616)-6929

Mo-25W-.1Zr-.03C	Mo-.01C
Mo-1.25Ti-.3Zr-.15C	Mo-.5Zr-.02C
Mo-5Cb-.02C	Mo-.5Ti-.07Zr-.02C
Mo-50W-.01C	W-.1Zr-.01C
W-30Mo-.01C	W-.5Cb-.01C
W-10Mo-.01C	W-10Ta-.01C
W-.01C	

TABLE 5
DIRECTORATE OF MATERIALS AND PROCESSES
EXTRUSION EQUIPMENT AND OPERATIONAL CAPABILITIES

<u>High Speed Horizontal Extrusion Press</u>	
Rated Peak Capacity	700 Tons
Rated Working Capacity	600 Tons
Working System Pressure	3000 psi
Ram Speed	up to 900"/min
Container Size	3 1/16" I.D. — 15" long
Container Temperature	1000°F max
Stem Size	3"

<u>Heating Stations</u>	
Ajax, Induction, 30KW, 4200 cycle	4000°F (argon)
Harrop, Globar, Semi-portable (Fire Curtain and Argon)	3000°F max 2800°F normal
Pereny, Globar (Argon)	2000°F max
Hevi Duty, Globar (Argon)	2500°F max

<u>Corning Glass No.</u>	<u>Ext. Temp. Range (°F)</u>
7570	1100-1500
8871	1250-1900
0010	1900-2450
7052	2400-3100
1720	2500-3200
7740	2950-3600
7810	Under study
7900	Under study

TABLE 6

WEIGHT PERCENT RECOVERY OF REFRACTORY ALLOYS
EXTRUDED AT VARIOUS TEMPERATURES AND RATIOS

<u>Mo-.5Ti-.08Zr-.02C^(d)</u>			<u>Mo-.5Ti-.08Zr-.02C^(e)</u>		
(a)	(b)	(c)			
2800	4:1	81%	2600	4:1	60.3%
3000	8:1	89.5%	2750	4:1	61.9%
3000	6:1	88.5%	2900	4:1	55.6%

<u>Mo-25W-.1Zr-.03C</u>			<u>Mo-25W-.1Zr-.02C</u>		
2600	4:1	70.5%	2600	4:1	76%
2800	5:1	63.9%	3000	5:1	79%
3000	6:1	94.5%	3200	6:1	89%
3200	7:1	80.1%	3600	8:1	89%
3200	8:1	87.1%			

<u>50Mo-50W-.01C</u>			<u>W-30Mo-.01C</u>		
2000	4:1	67.4%	2600	4:1	74.6%
2200	4:1	69.2%	3000	4:1	67.2%
3200	6:1	66.5%	3200	4:1	73.2%
			3200	5:1	51.4%

<u>W-.01C</u>			<u>W-15Mo</u>		
2800	4:1	81.6%	3000	4:1	79%
2800	4:1	55%	3000	4:1	71%
3000	5:1	70.3%	3200	4:1	Sticker
3000	6:1	69.2%	3400	4:1	Sticker

(a) Billet extrusion temperature (°F)

(b) Extrusion ratio

(c) Wt % recovery

(d) Harvey Aluminum report

(e) Giancola report

TABLE 7
EXTRUSION DATA FOR SINTERED Mo-W BILLETS

Material Identification	Ratio Temp (°F)	Press (Tons)	Ram Speed	Remarks
70% dense C. P.-Mo	6:1 2500	515	4.5 2.1	Broke in several pieces. Torn surface.
70% dense C. P.-Mo	4:1 2400	528	5.3 2.9	Severe tearing. Pine cone effect. Many small pieces.
70% dense C. P.-Mo	8:1 2400	620	3.1 Start	Stuck
97% dense C. P.-Mo	4:1 2100	474	7.0 5.4	Excellent surface. Sound rod.
97% dense C. P.-Mo	8:1 2400	633	16.8 5.2	Excellent surface. Sound rod.
97.5% dense W + 1% ThO ₂	6:1 3400	512	5.5 2.7	Very smooth surface. Sound rod.
89% dense W + 1% ThO ₂	4:1 3100	550	4.7 2.6	First half lateral cracking. Rough.
96.2% dense C. P.-W	4:1 3000	487	3.7 2.0	Smooth. Sound rod.
93.3% dense C. P.-W	4:1 3000	549	3.7 2.0	Smooth surface. Internal non-closure.
93% dense 50 Mo-50W	4:1 3000	571	11.8 5.9	Severe die wash. Sound rod.

THEORETICAL FORMABILITY

J. Bryars

Directorate of Materials and Processes, ASD

The major problem facing the aerospace industry today is the production of airframe components that meet the demands of increased environmental conditions. Significant is the cost of the newer metals. Added to this is the drastically reduced lead times required from engineering conception to delivery of the completed article. This problem becomes more acute when one realizes that very seldom is complete fabrication design data available for the engineer, and that the amount of funds available to develop design and fabrication information is greatly limited. These alone create a major problem, but we must not overlook the increasing complexity of the overall airframe structure.

The airframe industry needs to advance the state of the art for design fabrication using the new metals. To design and fabricate structures without sufficient data will only result in excessive scrap, inadequate tooling, and excessive handworking. "Theoretical Formability" provides the most direct means for solving the overall problem, and it is a must. It is simply an analytical method for predicting the forming limits of sheet metals using the properties of the materials. It directly provides verified fabrication design data in a very short time.

Let us take a look at some of the factors influencing the development of "Theoretical Formability." The exponential increase of material costs from that of the World War II aluminums to the space age refractories is important. It is evident that metals that will be fairly common in airframes five years from now, such as columbium and beryllium, have a cost increase over aluminum 300 and 500 times respectively. The material cost picture plus the great increase in application of the new metals forecast for the next decade, will have a tremendous influence on fabrication costs. In the Aerospace Industries "Trends Forecast," a survey conducted among airframe manufacturers has indicated the general materials usage for the next ten years. This survey showed that use of the super alloys and refractories relative to the aluminums and steels in 1960 was only 5 percent, but an increase to 30 percent was predicted by 1970. By multiplying the average cost of the super alloys and refractories at \$50 a pound for sheet materials, and their relative usages for 1960 and 1970, comparative cost factors for the three basic materials can be obtained. Although the super alloys and refractories produce only 50 percent of the total costs in 1960, they will contribute 90 percent of the total structural material costs in 1970. It can be realized that any saving in material, that can be gained by proper design and thus reduce scrapage, can be very significant.

Let us briefly review what has been done, to understand the forming of sheet metals, and review the progress made in the past two decades. We can divide this into two basic categories: (1) the practical experimentation type of forming development as evidenced by "cut-and-try" shop operations, and (2) the purely theoretical work accomplished by various universities and governmental agencies. Most of the work performed during, and immediately after World War II was on forming aluminum and magnesium. Practically all of this work was sponsored by the National Defense Research Council and the War Production Board. During the early fifties, very little work was accomplished. It was not until emphasis was placed on solving the problems associated with fabricating the titanium alloys, that industry realized that existing information was not adequate, and a major effort was initiated under the direction of the Office of the Secretary of Defense.

During all of these formability development years, there remained a cleavage between the purely theoretical and practical experimental type of work. Although considerable work was done by individuals in our universities and research centers in basic research very little practical application, specifically relating theory to shop practice, had been accomplished. To establish a relationship, a study was conducted to find the correlation between a metal's properties and processes to form it. The results of this study was the development of "Theoretical Formability." This concept "bridges the gap" between theory and shop. Two typical airframe parts are shown in figure 1 with their respective formability limit graphs in terms of the part's geometries. They are rubber formed stretch flange parts representative of bulkhead sections and deep drawn cylindrical cups. The graphs represent the geometrical limits of the particular parts for a given material. Other materials will have similar graphs. Parts with geometries falling outside the formability envelopes will fail during forming by either buckling or splitting. Those falling within the envelopes will form successfully. Limit graphs such as these can be developed for all forming processes and materials.

Actually there is nothing mysterious about "Theoretical Formability." Basically there are eight major steps necessary to develop formability equations. The procedure depends upon a thorough understanding of the forming process so that the parts and processes can be analyzed and the failure types determined. Then by determining the part geometries that relate to the failures we can develop the general failure limiting equations. Next, the equation is graphically portrayed, sample parts are selected and formed to empirically establish the position of the curve. At this point we will have established and verified a limiting curve for one process and material. We next establish a means to relate the properties of one material to another. These relation factors are called formability indices. Once these are established and verified, we can establish the position of curves for other material. Our last step is to finalize the equations into forms so that correlations between one material and another will be valid for selected geometrical and property parameters. Most important and this cannot be emphasized too much, these steps need to be done only once for each process. For a clearer picture let us take a specific part and process and step by step show the sequence and procedure used. As an example, let us consider deep drawn parts. The first step is to completely analyze the process and establish the major types of failures that will be encountered. For deep drawn parts, failure is evidenced by wrinkling of the flange due to compressive stresses applied to the part during forming, and splitting at the sides when the material is strained to the point that the metal separates. These failures are interdependent for this process and have to be considered together.

Next, we consider the part geometry and establish a relationship between the geometry and the types of failures for the process. In deep drawn parts we find the geometries of original blank radius R_0 , material thickness t , and part depth h are the primary ones.

These geometrical parameters will make it possible to develop equations that are a function of the geometry. The next step is to establish the basic equation of mechanics for the type of failure in terms of the part geometries. In considering buckling we find the basic equation for the critical buckling stress of the part is a function of the material stiffness, its deformation characteristics and the relationship of the flange height to material thickness. This basic equation is then expressed in terms of the part geometry. In a like manner, splitting is expressed as a function of the amount of ductility or stretch the material has without breaking. Although the general equations can become quite unwieldy, by proper analysis and selection of the primary and secondary variables, the equation can be simplified as shown in figure 2.

Because the equations just shown are not easy to correlate in their present form, they are then plotted on a graph as shown in figure 3. The graph at this stage gives only the shape of the curve, as represented by the equation, and the position of the graph can move as shown by the double headed arrows. This graphic expression of failure relationship, portrayed in terms of the part geometry, is used to select experimental parts to test the theory of the shape of the curve. The parts are formed and plotted to verify a curve for one material, establishing the limits of part size and shape.

The primary work established the shape of the limiting curve for a particular material. The next step is to establish a basis so that we can position the curves for other materials. To do this we will now find the function of the material's properties that will establish a relationship to the part geometries. For splitting failures the significant material property is elongation. In our particular case, elongation is the natural strain established by a 20 thousand gauge length in a tensile specimen. For buckling the ratio of Modulus of Elasticity to the Buckling Stress is the property which will establish the correlation we are seeking. These material properties are used as "formability indices" to relate one material to another as shown in figure 4.

Part shapes are now selected that will establish the position of the new curves for several different materials. The parts of the new materials are then experimentally formed and the results plotted on the graph. The theoretically established indices are then applied to the graph to adjust and establish the position of the limit curves for the new materials. The last step is to finalize the equations as shown in figure 5 that allow us to predict the forming characteristics of all materials for deep drawing. To do this the value of the constants are established in the equations that will be valid for all materials.

The preceding analysis shows that theoretical formability is actually an extension into practical terms of the theories concerning the elasticity and plasticity of metals. Completely new concepts have been developed, however, which are unique in metal forming. Vought Aeronautics has been working under an Air Force contract to extend the concept of theoretical formability to the following twelve forming processes:

Brake Forming	Rubber Forming
Dimpling	Sheet Stretch Forming
Joggling	Andro Forming
Spinning	Deep Drawing
Linear Roll Forming	Rubber Bead Forming
Linear Stretch Forming	Drop Hammer

This concept can be applied to any forming process, including the new high energy rate methods. But for this study, it was decided to apply the concept first to the more conventional forming process. Nineteen materials for formability analysis in the contract were selected to furnish a broad range of properties. This permitted the development of formability indices that can be applied to any metal. All important classes of aircraft materials are represented from aluminum to tungsten. The stainless steels, for instance, include the all-beta and the heat-treatable 6Al-4V; and the super alloys include both the nickel and the cobalt base types.

The current contract has already produced the results that were expected. The program has proven that the initial development of the formability limit equations and graphs are accurate. Not only are the graph shapes correct, but correlations show that the formability indices can predict the position of the graph for each material. This means that

the material properties obtained from simple tests can be used to predict formability limits. A major result of the program is the establishment of composite formability limit graphs. Graphs such as these allow the quick analysis of the comparative formability of the different materials.

Another significant result of the study is the development of design tables for various forming processes. Such information provides design engineers with the maximum and minimum dimensions of parts from various materials.

A third major result of the study is the development of predictability equations for the forming of future materials. These equations relate the geometry of the part to the properties of the various materials. To predict formability of future materials, all that we will need is the material's mechanical properties. These properties can then be substituted into the equations and limit graphs established. Experimental forming of a few parts will verify the graphs and give the engineer confidence in the design tables.

There are several benefits to industry that can be realized by the application of "Theoretical Formability." The development and qualification of design data for the engineer is important at a time when it is required. Within a matter of hours after the engineer has requested design data, preliminary information can be developed solely from the published material properties readily available. This information plays an important part in selecting a material for use by providing quantitative data that eliminates the guess-work. Within approximately 30 days, usually as soon as a limited amount of material can be procured and tested, complete design tables can be established, verified, and published. This information also provides the optimum processing sequence and material usage. Most important, the application of "Theoretical Formability" eliminates the major stumbling blocks such as limited design data, redesigns, improper material selection, and costly scrappage. Another benefit of theoretical formability is better designed parts. The most acceptable material can be selected, and, with a knowledge of the material limitations, it will be possible to design parts with fewer details.

Of major importance to manufacturing is the advantage gained from the proper selection of tooling and equipment required to fabricate the parts designed by engineering. By analysis of the part and material, the right forming process can be picked the first time, the fabrication sequence of temperature and material condition can be selected, and the proper tools with their optimum tooling materials provided. As an example, a part designed by engineering could have geometries that would allow the fabrication of the part by either drop hammer or mechanical die. Our first inclination would be to form by drop hammer from a cheaper tooling standpoint. But by having verified knowledge of the materials forming limitations for each process, we might find the part to be outside the limits for drop hammer and the selection of mechanical die operation, even though the tooling was more expensive, would allow us to form the part successfully the first time. This analysis will also tell us whether we need to form at elevated temperatures or not, and thereby guide selection of tools and tooling materials.

Up to now we have briefly reviewed "Theoretical Formability," its history, applications, and development, and summarized what is currently being done with some of the more direct benefits that will result. Although the work to date is a tremendous advance in basic understanding of forming processes, there still remains several areas in which we need to direct our efforts. The first area is the extension of "Theoretical Formability" to all sheet metal forming processes. The work just discussed under our present contract did not include some of the more complex shapes produced by several of the processes. These parts and processes need to be investigated to completely define each process

and all its applications. Several of the processes currently under investigation still require extension into more complex part shapes. Also there are several of the more conventional processes that have not been studied. As previously stated, this concept can be readily applied to the high energy rate methods, but to do this we need to explore these processes and develop a better understanding of their applications and limitations. We cannot afford the luxury of waiting until these processes are clearly defined through shop "cut-and-try" operations.

By the use of this concept, the tremendous saving in time, manpower, tooling, materials, and leadtime can be readily seen. If we multiply this by the number of prime and subcontractors in this country, this saving is manifold. We believe this is one of the most significant pieces of work being accomplished today. It is not only a break-through in the technology of forming metals but will result in tremendous dollar savings to the Air Force and DOD.

Our future program plans are oriented towards developing more scientific approaches to other metal forming processes and we encourage industry to think along these lines. We welcome your ideas, however, we also urge you to be prepared to provide some evidence of demonstrated feasibility or comparative results that we can more readily determine the merits or potential pay-off of your proposals. I'm sure that you realize we receive many new ideas from many sources. Those which are considered technically sound, and backed up with some evidence of significant improvement in results, have the greatest opportunity for support.

REFERENCES

1. ASD Technical Report No. 61-191, "Theoretical Formability." Wood, W. W.

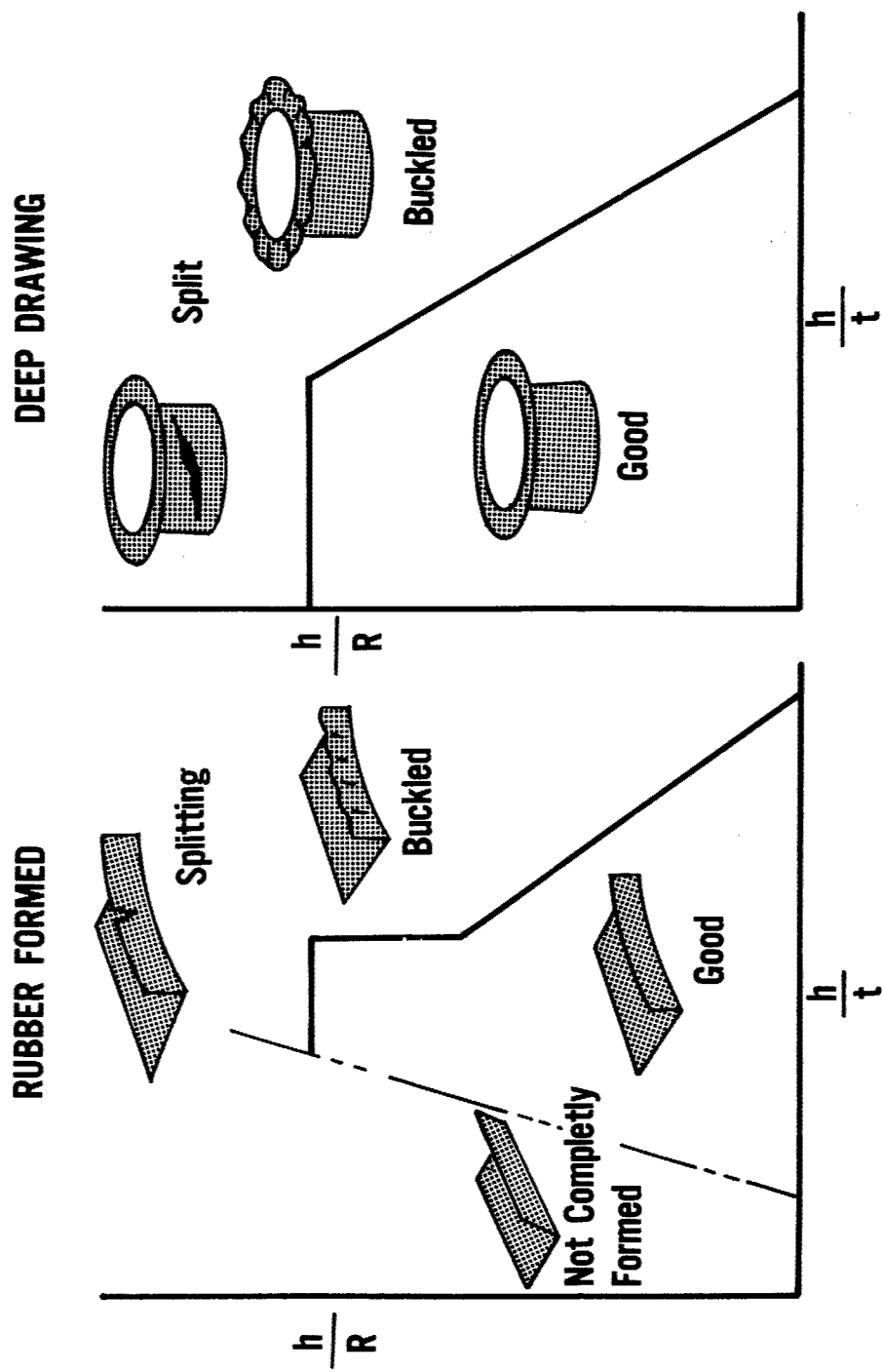


Figure 1. Typical Forming Limit Curves

BUCKLING

$$S_{CR} = \frac{K}{R_o^2 t} \left(\frac{Et^3}{12(1-\mu^2)} \right)$$

$$S_{CR} = B \frac{E}{(R_o/t)^2} = f \left(B \frac{h+R}{R_o} \right)$$

ELONGATION

$$e = \frac{R_i + h + (R - R_i) - R_o}{R_o}$$

$$e = f \left(C \frac{h+R}{R_o} \right)$$

Figure 2. The Basic Equation

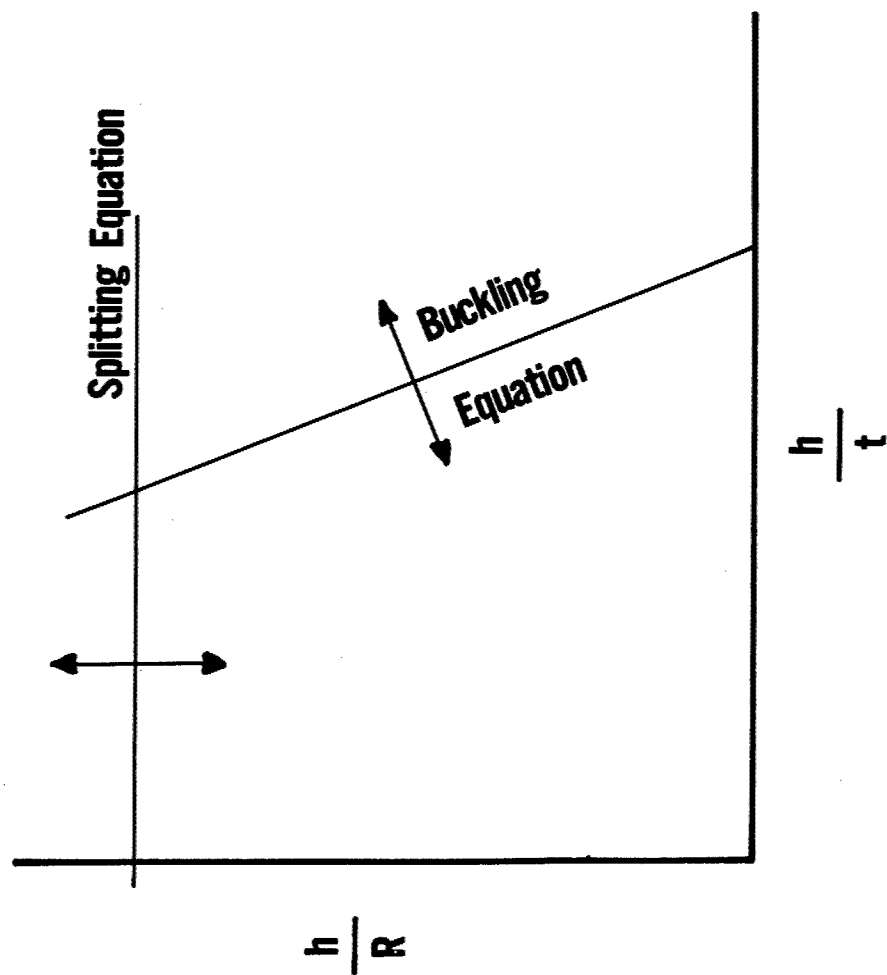


Figure 3. The Graph Shape

Splitting: Function of Elongation

$$\frac{h+R}{R_o} = f(e)$$

Buckling:

Function of

$$\left(\frac{R_o}{t} \right)^2 = f \left(\frac{E}{S CR} \right)$$

Modulus of Elasticity

Stress to Buckle

Figure 4. Formability Indices

SPLITTING CONSTANT

$$C = \frac{h+R}{eR_o}$$

BUCKLING CONSTANT

$$B = \frac{\left(\frac{R_o}{t}\right)^2}{\left(\frac{E}{S_{CR}}\right)}$$

Figure 5. Deep Drawing Predictability Equations

THE MECHANICAL BEHAVIOR OF MATERIALS

Chairman

Mr. W. Trapp

Speaker

Mr. D. M. Forney, Jr.

Panel Members

Lt. R. T. Ault

Mr. I. K. Ebcioğlu

Mr. R. F. Klinger

Mr. J. A. Roberson

Mr. K. D. Shimmin

THE MECHANICAL BEHAVIOR OF MATERIALS

R.T. Ault

I.K. Ebcioğlu

D.M. Forney, Jr.

R.F. Klinger

J.A. Roberson

K.D. Shimmin

W.J. Trapp

Directorate of Materials and Processes, ASD

Introduction

Nowhere in all the areas of advanced structural materials technology do we feel there is a more emphatic need for imaginative development of knowledge than in the area we have generalized here as the mechanical behavior of materials. It sooner or later develops that this side of a material's personality becomes the dominant criterion with which success or failure to meet requirements is ultimately measured.

The truth of this statement has surprisingly enjoyed little recognition until relatively recent times - within the last decade. At one time, off-the-shelf materials were abundantly available to meet the requirements of a new design. Today however, a new design is often limited by the lack of materials with the desired combination of properties.

In general, our drive for higher performance has cost us the luxury of having so called infinite life systems. Modern design is, almost without exception, based on the concept of a limited life of operation. The more complex the system and the more demanding the mission, the shorter the design life invariably becomes. Higher performance thus demands more efficient application of materials and at the same time introduces more severe environments in which materials must satisfactorily function.

The intrinsic mechanical properties of structural materials form only part of the story, however, and in the case of modern materials and applications, do not necessarily play the most important role. The optimum exploitation of materials properties through the knowledge of a material's compatibility with the operating environment and its continued performance therein, become key factors. Important here, then, is not only the knowledge of a material's ability to perform its assigned function, but the knowledge necessary to reliably predict its useful life early in the design stage.

This approach definitely has gone against the conservative tradition which characterized the materials as well as the design aspects of aeronautics of the past. Not too many years ago, as an example out of context, it was a firmly established opinion of most of those in the design fraternity that fatigue was a phenomenon observable in the laboratory but of no concern in a flight vehicle properly designed by static load criteria. Commercial as well as military equipment safety and maintenance records since the early 1950's certainly repudiate that opinion.

Because operating conditions have become so severe, we have had to pass from an era where "economic feasibility" dominated materials selection into one where "scientific feasibility" will dictate. It is necessary for the designer to pay considerably more attention to the sometimes independent-minded materials behavior than ever before. The characteristic feature of this trend in mechanics is the recognition that knowledge of the influence of imperfections of the submicroscopic, atomic and molecular structure of materials forms the basis from which the microscopic and macroscopic behavior of materials can be explained, predicted and exploited. Indeed, this is a time for an effective interplay between design and materials development.

The Metals and Ceramics Laboratory program of research in materials mechanics has been for several years carefully oriented to meet the needs of the changing requirements just described, both through internal programs and those performed under sponsorship. In general, the total program has followed along the guidelines outlined below:

1. Development of new and refined materials behavior concepts leading both to more efficient use of and performance of "standard" materials.
2. Maximum use of limited property materials through improved design concepts.
3. Development of failure concepts for "standard" and new materials.
4. Employment of new concepts to tailor multi-material systems with combined properties and develop knowledge of their performance characteristics.

In the discussions that follow, some of the programs being conducted by our Laboratory along the above lines will be described. For the sake of clarity, the discussion is presented in three parts each of which treat related areas of work. They are: materials dynamic behavior, creep, buckling and stress-relaxation and finally brittle behavior in materials.

Materials Dynamic Behavior

The area of materials dynamic behavior is recognized as being very broad, encompassing such occurrences as fatigue, damping, resonant vibrations, rapid loading, shock and impact. However, in this discussion, rapid loading, shock and impact will not be considered. The areas which remain might be categorized as dealing with forced stressing and stressing through resonance vibration.

Due to their very nature, forced vibrations are in most respects considerably easier to deal with than is the case of resonance vibrations. This is because the stress response of a resonant system may be highly non-linear and uncontrollable and therefore difficult to predict, whereas, forced vibrations follow a linear relationship between force input and resulting stress.

Fatigue

For many years, the fatigue phenomenon per se has been the subject of considerable research at all levels of observation, from a study of the basic mechanical metallurgy concepts to the accumulation of masses of design data. As for a discovery of an ultimate "solution of the fatigue problem", it seems unlikely that one will ever be found. It is clear now that the logical approach is one of reducing the problem to a level at which accurate control and prediction of performance is possible. In its simplest form the

fatigue process is at best, only partly understood. On the introduction of operating environments, the total process can be tremendously influenced by many factors and become very complex indeed.

There are many important studies in progress today to increase our understanding of the basic fatigue process. In general, the work is devoted to the two major steps recognized in the process, 1) studies of fatigue hardening of metals and 2) studies of fatigue fracture.

As for fatigue hardening, experiments by Broom and Ham (1) of Birmingham University in England have demonstrated the difference between fatigue hardening and tensile work hardening. Thin film transmission electron microscopy has shown how fatigue stressing uniquely produces prismatic dislocation loops and that it is these loops which contribute to the fatigue hardening process (2). Loop formation and the subsequent hardening are essentially completed after the first 100 to 1000 cycles of reversed stress if the stress is of such magnitude as to produce failure in one million or more cycles. It is these changes, incidentally, which are responsible for the rather large increases observed in resistivity which accompany fatigue stressing at low temperatures. If the fatigue stressing is carried out about a mean stress other than zero, it is known that an additional subgrain structure is superimposed on the hardened matrix. The formation of this structure is also essentially completed after the first 1000 cycles of stress have been introduced. The major changes observed in internal friction and damping are completed during this early hardening period as well.

The mechanism associated with ultimate fracture becomes operative in the small fraction of the volume of metal being stressed which softens. This softening occurs with the accumulation of slip, first on single planes, then intensified into striations or bands. Crack initiation then occurs in the work softened material of the bands. Our Laboratory is currently supporting studies of this cracking process. We have seen that the propagation of the crack is limited to the areas and direction of intensified slip and it passes from one band to the next by cross slip. Once it is better understood, it follows that the effect of various factors, such as vacuum, temperature, strain rate, and others, can be studied in greater detail.

A review of the effect of vacuum on the fatigue process, indicates the important experiments of Wadsworth and Huchings as being classical in demonstrating that most metals exhibit longer life (3). They found that the fatigue life of copper was 20 times longer and that aluminum exhibits a life 5 times greater when tested in vacuum. Experiments in our laboratory on PH 15-7 Moly stainless steel about the same time, as well as experiments by the Navy, illustrated similar results. The life exhibited by PH 15-7 Moly was on the order of 20 percent higher. The explanation of the phenomenon seemed to be in the reduced rate of crack propagation in the absence of oxygen. Later experiments by Wadsworth showed that the amount of oxygen present, and not the existence of a vacuum per se, was responsible for the crack propagation behavior and the fatigue life exhibited. The degree of increase in fatigue life was shown to be dependent on the number of oxygen molecules in a partial vacuum. It is postulated that a chemical attack of some kind occurs at the tip of a crack and that it occurs only while the crack is growing. Samples removed from the test chamber during fatigue testing were subsequently unaffected by the exposure.

Crack initiation, on the other hand, was found to be independent of the atmosphere. It seems that cracks are initiated very early in the fatigue life of a material, and that they grow quite slowly during the first 25 percent of the life (4). Many cracks are initiated

which never grow at all, only a few become large enough to be easily seen, and usually only one crack is operative at the time of failure. The situation is somewhat different in vacuum however, where it is found that even though the cracks grow at a slower rate, more of them are operative for a longer time.

It has been found that a vacuum coxing effect exists. That is, the fatigue life of a sample in air may be increased by first stressing the sample in vacuum for a short time.

As stated above, current experiments being performed to study the process of crack initiation and propagation are being extended to include observations of the influence of various amounts of oxygen. Experiments in our Laboratory are presently underway to observe this effect on the fatigue behavior of refractory metals since oxidation rates are so much higher in their case. It is expected that fatigue life here will be affected on the one hand by strain hardening or coxing, while on the other by more rapid oxidation in the propagating crack to decrease life.

The influence of temperature on fatigue behavior is another significant factor although it has not received much consideration so far in fundamental work. The room temperature process has occupied most of the attention focused on the general problem until recently since the introduction of temperature complicates matters tremendously. Aside from the general reduction of static elastic properties as might be expected with temperature, an increase occurs in the plastic component of the fatigue cycle and damage accumulation can take on a new dimension. Additionally, the damage process is susceptible to other alterations because metallurgical changes brought on by temperature, such as aging, local oxidation, stress relief, and the like, may change structure to which fatigue is sensitive.

Because of the increased plastic component of deformation under cyclic loading, fatigue at elevated temperatures is usually accompanied by some creep, the amount of mixing being dependant on the value of the preload. The specific amount of creep damage occurring during fatigue damage is a function of the temperature, the stress - both mean and alternating, the test frequency (the time at temperature and load), the nature of the test material, and probably other factors. Creep, on the one hand, is generally a continuous deformation process under load and occurs more abundantly at high temperatures. The rate of creep is influenced by many variables, but under a given set of conditions at elevated temperature, the rate controlling process is commonly considered to be the climb of dislocations. This implies that the glide of edge dislocations is hindered, or that the number of edge dislocations is limited. It seems likely that the initial rapid deformation which occurs after loading accounts for most of the unhindered dislocation glide.

The fatigue of metals, on the other hand, occurs at any temperature. The rate controlling process, if there is one, has to do with crack propagation since the specimen spends most of its total life in the cracked condition. Vast numbers of dislocations, vacancies and interstitial atoms are generated during the early part of the fatigue process. Their effect on crack propagation is not well established.

If we superimpose an alternating stress on a material exposed to creep conditions, or vice versa, we would expect an increase in the rate of damage in the material. However, this is not necessarily the case as is shown in figure 1. It is seen that the superposition of creep and fatigue stresses can sometimes promote a strengthening of the metal, apparently by means of a work hardening process. An exceptional degree of strengthening is shown in the case of Waspaloy by the shaded areas of the stress range diagram (5). Research in this area has been sparse, and what has been done has not been on a

fundamental level. Variables such as atmospheric effects, metallurgical instabilities, non-uniform stress distributions, and the like, must be considered in proposing a comprehensive failure mechanism.

Our Laboratory is supporting research in this general area. In this work, pure aluminum will be fatigued under various combinations of load and loading rate at temperatures ranging from room temperature to that of liquid helium. It is expected that this work will provide some insight as to how damage is partitioned between deformation due to stress activated and thermally activated dislocations and point defects. It may be found that loading rate is of fundamental significance as well as temperature, mean load, ultimate load, and the like. In addition to this, tests, are being made on long, thin-walled tubes of brass to establish the relationship between cumulative plastic strain and stress history. It has been found that plastic strain is dependent on stress path as well as the more obvious variables of temperature, maximum stress, number of cycles, etc. The culmination of this work should have fundamental significance in the field of theoretical and applied mechanics. The mathematical model should be an improvement over some of the older theories of classical plasticity.

Acoustical Fatigue

In regard to the question of resonant vibrations, one of the most powerful tools found to cope with attendant problems has been damping. For a number of years our Laboratory supported research which developed and refined damping concepts largely responsible for solutions being applied today. Our initial interest was stimulated by vibration problems associated with early jet engine designs, particularly critical in the case of turbine buckets and compressor blades. Here, materials self-damping, as well as Coulomb or friction damping at connections, offered an important solution.

In the early 1950's the sudden development of the acoustical fatigue problem gave impetus to a structural concept of damping in which non-load carrying materials, having very high damping characteristics, would be used in a structure to reduce resonance stresses in loaded materials rather than the loaded materials provide their own damping (which is insufficient to cope with the acting energies).

Actually, since the early days of aircraft design, there have been cases of airborne excitation of structures such as flutter of wings and control surfaces or excitation of fuselage components generated by propellar pressure pulses. However, in these cases only under specific and rare circumstances was there enough energy available to cause structural damage of the energy absorbing structure.

With the advent of supersonic flight and high thrust propulsion systems, pressure pulses or noise levels became high enough to excite continuously and maintain serious structural vibrations. Structural failures caused by these vibrations have been termed acoustical or sonic fatigue failures, implying that their source is airborne energy in the form of pressure fluctuations. Figure 2 shows typical examples of this type of failure. These pressure fluctuations may either be periodic or random. If they are periodic, excitations are relatively easy to cope with by means of appropriate frequency adjustments of the receiving structure or use of the interference phenomenon of sound waves. However, the reduction of random excitations or elimination of random resonance fatigue, associated with high intensity noise, cannot normally be avoided by the same means because both jet exhaust and boundary layer "noise" spectra have a frequency bandwidth which includes most of the natural frequencies encountered in conventional structural components of aerospace vehicles. Figure 3 shows a typical sound-pressure-frequency

distribution for pertinent systems and sources to illustrate this. Figure 4, in which power level measurements made on an F-100 aircraft are plotted over Mach number, makes a comparison of in-flight noise.

Since random resonance is therefore a most difficult problem, the gathering of information on noise sources and characteristics of the environment they produce, which is essential in design of exposed structures and in prediction of structural life, has been one of our efforts in this area in recent years.

A great variety of aero and thermodynamic conditions are involved in noise generations; however, since this subject is amply covered in earlier publications (6, 7) it will not be treated in the present paper.

The general problem of acoustical fatigue can be broken down into three component parts:

- 1) the acoustic environment to which the structure is exposed,
- 2) the response of structures to this environment, and
- 3) the structural fatigue life at specified cyclic stresses.

Our chief activities in recent years besides the study of the acoustic environment have been concerned with the response of structural components and the increase of acoustical fatigue life.

The main difficulties in this work is posed by the fact that most structures have a non-linear response characteristic. Panels, for instance, display a high degree of non-linearity in stiffness at large amplitude, which causes their natural frequency to be highly dependent on amplitude.

Considerable knowledge has been gained in recent years and more accurate expressions of acoustical fatigue strength derived through experimental studies of response characteristics and the behavior of basic components as well as response correlation studies on a combination of these components or whole structures under acoustical service and laboratory conditions.

Four properties of materials and configurations govern acoustical fatigue strength: 1) random materials fatigue strength, 2) natural frequency of the configuration, 3) static stress produced by unit pressure, and 4) structural damping. It is obvious that the last two offer the greatest potential for an improvement. Significant gain can be realized in acoustical fatigue strength by careful detail design in order to minimize the maximum statically-induced stress. However, the conventional design concepts are inadequate to deal successfully with the fatigue problem associated with resonance amplification. Although "beefing-up" a structure for increased strength and stiffness has "fixed" resonance fatigue difficulties in some cases, this approach cannot be considered a long-term engineering solution. Not only is the weight and cost penalty large in this approach but it is also totally inadequate to meet the problems encountered in many of the new types of aero-space vehicles. Consequently, the utilization of the fourth property, structural damping, as an engineering property to control acoustical excitation is a necessity. In the future it will still be necessary, of course, to reduce the maximum statically-induced stress by using heavier members or build-ups. However, if maximization of damping is also considered to be a design objective in addition to the static strength

increase, then a much larger gain in acoustical fatigue strength can be realized than using either criterion alone.

Whereas in the past the damping of a structural assembly may have been increased by the addition of separate energy absorbing means such as use of dashpots or surface layer treatments such as coatings and tapes, this approach no longer provides an engineering solution for the newer types of configurations and acoustical conditions. Instead, the design concept of optimizing a configuration for maximum inherent structural damping must be emphasized. The experimental and analytical knowledge which we gained through our research efforts in the recent past on the major sources of inherent structural damping such as hysteresis in structural materials, interface slip and interface viscoelastic shear, has now reached a point where application to structural design is practicable.

Of these possible damping types only the interface viscoelastic shear damping was found to be reliable and effective enough to make a worthwhile contribution to the increase of the acoustical fatigue life of structures. And it is for this reason that our Laboratory has devoted considerable effort to the realization of viscoelastic damping both in optimized structural configurations and in surface layer additions.

Figure 5 shows some of the basic ideas used in this concept. Sketch a) of this figure demonstrates interface shear damping of a sandwich panel; Sketch b) shows shear damping at a panel connection initiated by membrane action; and Sketch c) shows an example of panel damping by surface layer addition with restraining metal foil.

Looking at the overall acoustical fatigue problem, it becomes apparent that knowledge of its individual components - noise environment, response and damping-is necessary for a satisfactory solution and the continuation of research along these lines is in order.

Viscoelasticity

The very early efforts to seek improvement in the dissipative character of structures through damping treatments with viscoelastic media were largely by trial and error. To optimize an application however, it became evident that only by approaching a solution on the basis of viscoelastic theory was an effective result to be had.

In the last decade a great deal of work has been done in the development of linear viscoelasticity of a homogeneous and isotropic material and many technologically important problems have been solved. However, if viscoelastic effects appear in a non-linear manner, a solution becomes very difficult and it seems likely that only the simplest problems can be handled completely satisfactorily. In many cases, linear viscoelasticity can provide a sufficiently good approximation to the solution of non-linear problems and offers numerous mathematical methods of attack. Because of the basic difficulties encountered in non-linear analysis, it has become extremely important to exploit linear viscoelasticity theory to the utmost extent.

Our Laboratory is providing support of research to extend, where possible, certain aspects of linear viscoelasticity. This work is divided into two parts. First, research is progressing to extend the state of the art with particular reference to Lagrangian Methods. The partial mode analysis is emphasized and material anisotropy is being considered. The second part of the research considers specific cases of current technological interest, including viscoelastic damping phenomena, sound and energy absorption in laminated beams, plates and shells. Although many applications can be described as direct applications of the basic theories, additional work will be necessary to clarify

approximate procedures that can be used in the solution of engineering cases. Problems involving beams, plates and shells are being studied with various boundary and loading conditions as well as different material properties.

Dynamic Modulus

In the stress analysis of vibrating members, it is usually desirable to know the dynamic modulus of elasticity which is higher than the modulus of elasticity obtained in static tests. Several explanations have been given for this difference. Fine (8) offered an explanation on the basis of thermodynamic behavior at various speeds of stressing, reasoning that when a tensile or compressive stress is applied to a material, there is a production or absorption of heat. In static tests, time is sufficient for a heat exchange with the surrounding medium so that the test is isothermal. However, time is not sufficient in a dynamic test for such a complete heat exchange so that this test is considered adiabatic. Fine expressed the relationship between isothermal and adiabatic modulus values as

$$\frac{1}{E_{is}} - \frac{1}{E_{ad}} = \frac{T \alpha^2}{\rho c_p}$$

where:

E_{is} = isothermal modulus of elasticity

E_{ad} = adiabatic modulus of elasticity

T = absolute temperature

α = coefficient of thermal expansion

ρ = density

c_p = specific heat at constant pressure

Zener (9) has explained the difference in terms of the time dependence of the relationship between stress and strain. He showed that there is an instantaneous stress-strain relation - called the "unrelaxed elastic modulus" and another relationship occurring after a finite relaxation time called the "relaxed elastic modulus" which has a lower value than the unrelaxed modulus. Hence, the behavior of a material depends on the speed of stress application with respect to the mean relaxation time for the material. In dynamic modulus tests (or for example, in the case of acoustical vibrations), the stressing speed is high enough for the unrelaxed modulus to be operative.

Our Laboratory has developed apparatus for making dynamic modulus measurements at room and elevated temperatures in either a longitudinal or bending mode and has recently published data for a representative group of materials (10). The sensitivity of the apparatus is such that the effect of metallurgical changes, such as alloying, aging, recrystallization, etc., on the dynamic modulus have successfully been observed (11). In figure 6 is shown examples of the influence of some representative metallurgical variables. Our current apparatus development work is geared to higher temperatures in a

set-up which excites the bending mode of a sample. The apparatus will provide a vacuum at temperatures to 1600°C for additional research on mechanical metallurgy questions.

Cumulative Damage

Forced as well as resonance related structural vibrations can be produced by energies generated either mechanically or aerodynamically. The mechanically generated energies are almost exclusively transmitted through the structure itself whereas aerodynamically generated energies are either structure borne, or airborne when they originate from gust or maneuver activities. However, if they originate from turbulence created by jet engine or missile exhaust or boundary layers they are almost entirely transmitted by air in the form of pressure pulses (noise).

For several years our Laboratory has been actively concerned with devising a more realistic account of the damage which accumulates due to different stress levels and histories imposed by the spectra of such vibrations.

In recent years use of Miner's linear damage rule (1946) has been almost universal in aeronautic design circles. However due to its inability to cope with more complex stress histories and mixing of extreme values of stress, interest grew in a more descriptive damage criterion. Research work of Freudenthal and Heller (12-16) has developed conclusive evidence that "stress-interaction" takes place which appears to be responsible for the discrepancies in the linear damage hypothesis. In other words the effect of introducing high stresses is to increase in some materials the potential damage of heretofore "non-damaging" low stresses so that damage proceeds under low-level stressing which is not accounted for and causes "premature" failure. On the basis of this damage mechanism Freudenthal devised his semi-empirical quasi-linear damage rule which is illustrated in its effect in figure 7.

The noted deviation from a constant rate of damage accumulation, described by a linear rule, is due to the dependence of the damage rate on the applied stress levels which themselves are varying randomly. For a stress sequence containing predominantly high stresses and consequently having lower life, a smaller degree of stress interaction occurs because of an abundance of cyclic plastic deformation taking place. Stress spectra containing mostly low stress peaks of similar value in considerably greater quantity than higher peaks, result in a more linear damage accumulation rate. Of course, the nature and extent of the deviation from linear behavior varies with the material considered and the "shape" of the spectrum. Now that basic concepts have been established the more complex conditions representative of actual service conditions are being introduced such as effects of mean load, structural redundancy, type of loading, etc.

Since most of the load spectra to which aeronautical systems are subjected are largely random in nature, which means they do not occur in an established sequence, the problem is largely a statistical one. The aim in our work towards the solution of the problem is the establishment of a more uniform cyclic loading with a damage potential equivalent to the given random load spectrum. The statistical part of this problem is at present being conducted for us by Dr. Weibull of Sweden (16). Dr. Weibull also in recent years has been studying a problem for the Air Force which is of particular interest to aircraft structures test people. Prompted by the lack of large numbers of specimens for fatigue reliability tests of components and whole structures, studies were made of the possibilities of arriving at a probability of failure with an accuracy sufficient for the prevailing case, using a small number of test samples. Encouraging progress was made which allows interpretation of fatigue test results from a small or reasonable number of test

points distributed evenly over the whole range of the S-N curve (18, 19). Also under consideration are the problems of small sample statistics for extreme values such as are prevalent at the so called fatigue limit.

Reliability

When one considers the total picture of the reliability of a complex, long but finite life mechanical system, the task of making an accurate quantitative prediction of life seems awesome, and at first glance, it seems hopeless that one is possible without introducing safety factors which are orders of magnitude too broad. The overall deterioration of a finite life mechanical system is governed by so many individual deterioration mechanisms with different rates, each perhaps sensitive to various changes in operating environment, that system failure can often appear to be "chance" failure. However, this has generally been shown to be fallacy and that the prediction of fatigue life for example, can be put on firm statistical grounds (20).

Although the methods of stress analysis have been greatly improved and refined through the use of computers, and our knowledge increased in the use of materials, the methods of safety and reliability analysis have not improved significantly, and in general are still based on the use of more or less arbitrary safety factors that can neither be justified by rational argument nor related to a probability of failure (20). In short, the principal tool needed is an analytical technique which would first establish the expected life of a system, related to a probability of failure and a risk function, and which could re-estimate a new value of life when a new set of operating conditions are introduced, such as a change in the mission profile of a flight vehicle from the original design specifications. Important research along these lines has been underway recently under the support of our Laboratory showing considerable promise (21). The first phase of development involved the establishment of the risk function describing the increasing risk of fatigue failure as damage accumulates together with the evaluation of the chance of "premature" failure from a sudden high overload. This phase was based on laboratory test data. This work is continuing under plans for studying data from extensive aircraft structures test programs and flight records both from this country and several foreign countries and making final adjustments in the statistical theory.

Creep, Buckling and Stress-Relaxation Behavior of Materials

Creep

In high performance systems, structures are subjected to stresses at elevated temperatures over varying periods of time. Under these conditions the materials from which the structures are made undergo creep deformations or are subject to the phenomenon of stress relaxation. Designers of structures for such applications are interested in producing designs with emphasis on reliability and most efficient use of light weight structures in order to maximize performance. In order to optimize the design it is necessary to predict the creep and stress relaxation behavior of materials, under varying conditions of stress and temperature, within fairly close limits of reliability. It is also necessary that such predictions be based on test data which is obtained under more limited conditions of stress, temperature, and time than those incurred in service. Practically all data, on which to base predictions are obtained from creep tests conducted under conditions of constant load and constant temperature. Attempts in the past to develop purely empirical formulations to predict creep behavior of materials under varying stress, and temperature histories have met with little success. And it has been shown that the

conversion of creep data into relaxation data does not provide reliable information on the stress relaxation behavior of materials. Since the empirical approach to prediction of creep and relaxation behavior has not been successful, it is necessary to acquire more fundamental knowledge in these areas, by using a physical or phenomenological approach to determine the basic laws governing such behavior, and to use these laws as a basis of predicting design criteria.

After a rather unsuccessful attempt several years ago to establish empirically the creep behavior of engineering alloys under conditions of intermittent stressing and thermal cycling, our Laboratory initiated a basic study of creep behavior based on a physical approach. An investigation of the creep behavior of pure polycrystalline aluminum was initiated. The pure aluminum was selected as a starting point because of its relatively simple structure and the fact that mechanisms such as aging would not complicate the analysis of creep behavior. It has been established that the creep rate of the high purity metal may be represented by the equation:

$$\dot{\epsilon} = S e^{-\frac{\Delta H}{RT}} \phi(\sigma) \quad \text{Eq. (1)}$$

where:

S is a structure factor dependent on stress and strain history

ΔH = activation energy for creep

R = gas constant

T = absolute temperature

$\phi(\sigma)$ = function of stress

σ = stress

Initial work in the investigation studied the effect of temperature on the creep behavior of pure aluminum. By holding the stress constant and introducing slight changes in temperature, the relative creep rates before and after the temperature step were used in equation (1) to determine the activation energies for creep (22-24). Figure 8 illustrates the activation energy for creep of high purity aluminum in the temperature range 0 to 900°K which were established in this manner. The activation energy for creep increases from about 4000 to 28,000 cal/mol over the range 78 to 240°K, in a manner which has been explained as simultaneous operation of the Peierls process and cross-slip; from 240 to 370°K the activation energy remains constant at the 28,000 cal/mol value for cross-slip; it then increases to 35,500 cal/mol and remains at this value for all temperatures above 500°K. This value of 35,500 cal/mol is associated with the process of dislocation climb.

Having established the effect of temperature on creep behavior of pure aluminum the next step was to attack the problem of determining the contributions of stress and the structure factor on creep over the temperature range of application of the material. It has been demonstrated (25) that during primary creep where S , the structure factor, is changing constantly with strain, the stress effect cannot be represented by a unique

function $\phi(\sigma)$ but is also implicit in S . This result has complicated the analysis for the effect of stress upon the creep rate.

During creep under cyclic stressing, recovery or softening of the material may occur during the period of the cycle when the stress is reduced. The manner in which recovery affects the creep rate must be investigated throughout the range of temperature of application of the material.

In order to make use of the basic information on creep, which is being obtained on a pure material, it will be necessary to investigate the effect of alloying additions in engineering materials on the basic factors involved in creep.

At the present time our program in the investigation of fundamentals of creep behavior includes studies of the following nature:

1. A study of the recovery of creep resistance in the cross-slip region of temperatures.
2. An investigation of the effect of stress changes in the cross-slip region of creep.
3. Research on the effect of alpha solid solution alloying on recovery.
4. A study of the effect of alpha solid solution alloying on the creep curve following a drop in stress.
5. A study of dislocation locking in alpha solid solutions of aluminum.
6. Research on the mechanism and rate of sub-boundary movement.
7. A study of the effect of stress increases on the permanent plastic straining during primary creep in the dislocation climb region.

The trend of work in the area of fundamental studies of creep behavior is oriented toward progressively more complex problems eventually to deal with engineering cases. The transition must be slow however so that we can carry the fundamental knowledge with us.

Since at best it may be quite some time before we have sufficient fundamental knowledge to be able to predict reliably the creep behavior of materials, most current designs consider the commonly available constant load-constant temperature creep information when it is necessary to consider the effects of time at elevated temperature. Even in the case of common test information, we are faced with a gap in the knowledge when it is necessary to design for extremely long life at elevated temperatures as is the case in supersonic transport aircraft, manned satellite systems, engines for sustained operation, etc. Practically all available creep information on materials of interest in the design of such systems is limited to information determined at times of 1000 hours and less. Since the acquisition of creep information for extremely long time periods, up to 30,000 hours and longer, is quite expensive and involves unacceptably long lead times for materials, it becomes necessary to develop a reliable method of predicting long time creep behavior of materials from relatively short time tests. Efforts in the past in extrapolation of long time creep data have involved: First, the use of fundamental knowledge to predict behavior, and second the use of various graphical presentations in the correlation and extrapolation of creep data. We have seen earlier that the state of the art in the fundamental knowledge has not advanced to the point where it may be used in the prediction of creep

behavior of engineering materials. Most of the graphical methods of extrapolation which are based on a master curve associated with some time-temperature parameter fail in the extrapolation of long time creep data because they fail to consider materials instabilities.

Our Laboratory has initiated a program which by means of a phenomenological approach will develop an extrapolation method for predicting long time creep behavior which considers the various materials instabilities encountered in engineering alloys. The program will also include a study of the inherent scatter of creep deformation and rupture life data to establish the reliability of extrapolated data.

Stress-Relaxation

The characteristic of most metals to relax part of an applied load at elevated temperatures due to a form of creep has become a major concern to designers of high temperature systems. Phenomenologically, the process of stress-relaxation is explained as the conversion of the initial elastic strain in a material into irrecoverable strain of the same magnitude through inelastic deformation of the medium under decreasing stress. The reliable evaluation of the relaxation behavior is rather cumbersome because of the difficulty of applying initial strain rapidly enough to ensure elastic response and subsequently controlling the strain accurately enough during the test. Because of these difficulties and because of the relative simplicity of creep testing equipment it has been a widespread practice to interpret the relaxation characteristics of a material from creep data. The assumption is made that the inelastic strain, which is produced during a relaxation test, proceeds by the same mechanism as the creep test. Thus, neglecting the effect of creep-recovery, the rate of stress decay is expressed as:

$$\dot{\sigma} = - E \dot{\epsilon}'' \quad \text{Eq. (2)}$$

where

$\dot{\sigma}$ = time rate of change of stress

E = the elastic modulus

$\dot{\epsilon}''$ = time rate of change of inelastic strain (which is a function of time, initial strain and stress)

Using this relation, the relaxation function $\sigma(t)$ can be obtained by simple, though frequently cumbersome, integration.

Through our support, Professor Freudenthal analyzed the conventional approach to the conversion of creep data into relaxation data, and he demonstrated several discrepancies arising in this conversion with the aid of Eq. 2 (26). First, creep tests are practically always performed under constant load and therefore (because of lateral contraction accompanying extension) under slightly increasing true stress ("loading"), while stress-relaxation of course takes place under decreasing stress. In other words, creep in a crystalline aggregate proceeds under conditions of changing structure, while relaxation proceeds with practically no structural change. Therefore, part of the deformation process which occurs in the normal creep test is blocked because of the decreasing stress during relaxation ("unloading"). The temporary blocking of the creep rate by a decrease in stress has been confirmed experimentally by several investigators (27-29). As a result of this blockage, the use of converted creep rates will result in the prediction of

higher relaxation rates than actually occur. A second discrepancy arises from the use in the conversion process of the elastic compliance rather than the sum of the elastic and tangent compliance for a given strain on the true isochronous stress - strain diagram (not derived from creep data). A third discrepancy arises from the neglect of the effect of creep-recovery in the conventional procedure.

Freudenthal has approached the problem of relaxation on the basis of an assumed "mechanical equation of state" leading to a four element non-linear viscoelastic model which is assumed to be the simplest possible representation of the stress-strain relation of a volume-constant material (30). In the case of linearized materials, the required elastic and viscous coefficients necessary to solve the model equations can be obtained from constant stress tests and directly applied to cases of continuously changing stress. In real non-linear materials the conversion procedure becomes more cumbersome. Experimental evidence has been obtained to illustrate the ability of the model to represent actual material behavior under linearly decreasing stress, constant stress and linearly increasing stress. Figure 9 shows the agreement between theory and experiment for 2024-T4 aluminum alloy tested at 375°F. This research is intended to establish a workable relation between the physically and mathematically simple condition of linear stress variation and the experimentally difficult condition of true stress-relaxation in which the strain has to be kept constant. Further, the effect of intermittent temperature, multi-directional stress and boundary conditions are to be studied.

Our Laboratory is performing an internal research study on relaxation behavior in support of the above work. A standard commercial relaxation testing machine has been modified to incorporate a specially designed precision extensometer capable of sensing and recording strains of the order of one micro-inch. Using this equipment, the stress-relaxation behavior of high purity recrystallized aluminum is being investigated in the temperature range of 75° to 200°F. The objective of the program is to evaluate the temperature dependence of the relaxation rate, and to compare the relaxation activation energy with activation energies obtained for creep of aluminum in the same temperature range. It is hoped that additional information on relaxation mechanisms will be learned.

Thermal Deflection and Buckling

The desire to operate flight vehicles at higher velocities has brought with it a host of new and complex problems to the structural designer and analyst, not the least of which is the introduction of the temperature parameter.

For example, aerodynamicists have shown experimentally and theoretically that a detached curved shock will always exist in the upper stream of a conventional wing with a round leading edge at all supersonic speeds. Down stream of the curved shock the flow is subsonic and may extend to the trailing edge. It is then evident that this subsonic flow will produce a great deal of drag, and it is the reason that supersonic wings are made comparatively thin with sharp leading and trailing edges, which in turn have given rise to new structural problems.

A second problem is the thermal heating of the structure due to aerodynamic friction, requiring that plastic flow and creep conditions be considered in the design.

Thirdly, non-uniform temperature distributions in the structure will cause thermal stresses in addition to the stresses from mechanical origin. A non-uniform temperature distribution may easily be developed in a structure as complicated as a flight vehicle wing even under uniform heating rates. This problem is more complicated in supersonic flight since leading edges of the wing are exposed to much higher rates of heating than

the rest of the structure. Therefore, special attention has to be given to the structural design of the leading edges for supersonic flight.

Finally, the instability of the structure in the presence of thermal stresses has to be considered. For example compressive stresses will always be developed in a panel or shell under non-uniform temperature distribution even if it is not supported. Instability of the structure will reduce the overall strength but may not yield the overall collapse because of the additional constraints. However, the buckling of the external surface of a flight vehicle will reduce the aerodynamic performance due to waviness which of course is not desirable.

In order to overcome difficulties mentioned above the structural designer has to make the best choice of available materials for various operational conditions, and materials specialists must continue to develop new materials with emphasis on better high temperature characteristics. Another line of attack is to find the best combination of different materials to form an integral unit to partly satisfy all the required conditions. For this purpose sandwich panels have been used in elevated temperature, high strength and high stiffness applications for various flight vehicles. Their light core reduces weight and increases stiffness properties compared to any high strength sheet material construction. Furthermore, better performance could be obtained from sandwich panels if their faces are chosen of different materials and thicknesses.

Unfortunately, presently available sandwich panel theories can not be used for arbitrary temperature distributions and dissimilar face materials. For this reason, a general small deflection theory for a sandwich panel with an orthotropic weak core has been developed as an internal research program in our Laboratory and has been applied to various practical problems (31). It is shown that general thermoelastic equations for a sandwich panel consist of five differential equations in terms of the displacements of faces and appropriate boundary conditions. These equations have been reduced to the solutions of two independent systems of equations, with a suitable transformation of the unknown functions. These equations are shown in figure 10 in generalized form. The explanation of notations are omitted here but fully explained in reference (31). One of the systems consists of two differential equations, and its solution determines the components of the stresses in the plane of the panel. A second system consists of three differential equations and their solutions determine the deflections and corresponding displacements. The latter differential equations can be reduced to the equations derived by Reissner (32), Hoff (33) and Chang - Ebcioglu (34) under particular assumptions.

Other research supported by our Laboratory has been centered on the use of short-time buckling theories for predicting creep buckling failures of longer time duration through the use of more abundant short time data. It has been found that end shortening measurements, heretofore generally neglected in most other investigations, are significant for relating the creep buckling behavior of columns to the creep properties of the column material (35). Center lateral deflection measurements also exhibited a definite relationship with failure time data. It is now considered possible to extend short time theory to creep buckling by considering the strain value corresponding to the short time buckling stress as the critical strain in creep buckling (36). In general, additional improved analytical techniques for describing and predicting elevated temperature structural behavior are needed.

Fracture and Brittle Behavior in Materials

In discussing brittle behavior it must be kept in mind that there is no universally acceptable definition for such behavior and the identification of "brittle fracture" must be made for each particular case under consideration. This implies that there are many factors which influence the extent to which a fracture is brittle. These factors range from a minute consideration of the mechanics of microcrack nucleation to the more gross consideration of continuous stress state. If a careful examination is made, it is generally possible to associate with "brittle fracture" some degree of yielding or plastic flow. Under these conditions it is not unreasonable to study and define "brittle fracture" as it competes with plastic flow. Our programs then are aimed toward identifying some of the factors which influence "brittle behavior" and explaining how these factors contribute to "brittle behavior" separately or in combination. They are primarily concentrated on three categories of materials - high strength to weight metals, refractory metals and ceramic type materials. The types of approaches being used are to study external parameters which induce brittleness such as state of stress, chemical environments, and low temperatures, and also internal material parameters such as grain size, impurity content, and dislocation interactions, as they effect brittle behavior in both metals and ceramics.

State of Stress

One of the first factors recognized to contribute to the embrittlement of metals was the effect of stress state. Many investigators have studied the effects of stress state as induced by notches, on the fracture of metals but, as yet, these effects on the strength properties of a metal part are only partially recognized.

A theory of brittle failure that is now well known and universally recognized was developed 40 years ago by Griffity (37). The Griffity crack concept, originally proposed for the failure of glass, has since been modified by Orowan and Irwin and his co-workers (38), to apply to structural metals. The Griffity-Irwin theory, however, applied only to sharp cracks and has no bearing on the behavior of a material in the presence of a stress concentration of a definite magnitude. Therefore, in order to better understand the nature of fracture of engineering materials in the presence of mechanical notches a program supported by our Laboratory has been underway to study the effect of stress state on the strength properties of sheet materials (39).

The primary purpose of this program was to study the principal factors known to affect the strength of sheet materials in the presence of stress concentrations as caused by notches. These principal factors are the strength level of the material, and the stress distribution along the notched cross section. Significant in this study was the fact that the stress concentration factor calculated according to Neuber-theory was held constant. On the other hand, a variable which has received little consideration in previous studies, the stress gradient, has been varied for different notch depths and section widths. The stress gradient at the root of the notch was determined analytically from the notch geometry according to elastic theory.

The results of tests on an extremely brittle titanium sheet alloy indicated that the stress gradient is the predominant factor that influences notch strength. For a truly brittle material, it appears that the stress concentration factor, the depth of a notch, and the specimen width are significant only insofar as they contribute to the magnitude of the stress gradient and the maximum stress at the notch root. This is illustrated in figures 11 and 12.

As a result of these findings further studies are being conducted to determine the effect of stress gradient on the strength of brittle sheet materials.

The results of these studies are hoped to contribute to the understanding of the effects of strain state and stress gradient on the fracture of both brittle and ductile materials.

In this area of investigation another program is being conducted to study fracture initiation in notched tensile specimens. The effect of notch severity and grain size on the flow pattern in notched sheet tensile specimens of commercially pure molybdenum are being studied. Zones of initial yielding and patterns of plastic flow accompanying fracture are being analyzed as an elastic-plastic interface in order to elucidate the location and mode of fracture initiation.

Stress Corrosion Cracking

Included in the subject of brittle behavior in materials is the area of environment induced brittleness. By environment induced brittleness we mean the apparently brittle failures which occur in normally ductile metals in the presence of a chemical environment. These failures usually occur as delay type failures when the metal is under applied stress in the environment. Included in this area are the subjects of hydrogen embrittlement, surface absorption, liquid metal embrittlement, and stress corrosion cracking.

Although all of these causes of embrittlement are important, the area of stress corrosion cracking is probably the most troublesome at present, in terms of failures in flight vehicle structures.

Although the phenomenon of stress corrosion cracking has been with us for the past 50 years, we still know very little about the basic nature of stress corrosion cracking. In order better to understand the effects of certain environments on various structural materials and their related mechanisms several research programs are underway.

In laboratory tests, titanium alloys have been found to be susceptible to stress corrosion at temperatures between 550°F and 900°F and under stress in the presence of inorganic chloride salts. Limited experience in the laboratory suggested that other metallic materials such as nickel, cobalt-base alloys, and aluminum may also be susceptible to this type of corrosion. The purposes of the program (40) were: (a) to learn more about the chloride salt stress corrosion of titanium alloys with particular emphasis on how the protective character of the oxide film is lost; and (b) to explore the susceptibility of representative jet aircraft structural materials to elevated-temperature stress corrosion in the presence of chloride salt, and jet engine fuel or fuel residue.

In regard to the elevated-temperature chloride salt stress-corrosion of titanium alloys, experiments were conducted to determine whether the protection of the oxide film is lost by direct chemical reaction, or by dissolution, i.e., oxygen diffusion into the base metal. These experiments showed conclusively that film protection is lost not by dissolution but by chemical reaction of the chloride salt with TiO_2 .

Several of the alloys investigated were found to be sensitive to stress corrosion cracking in the presence of a salt environment, at both room and elevated temperatures.

No detrimental effects of any of the test materials were found in the presence of JP-4 fuel, tested either in tension static fatigue at room temperature or in elevated-temperature creep tests.

As a result of these findings, further studies are being conducted in order to determine the basic nature of the stress corrosion failures in the alloys investigated.

Before completely satisfactory solutions to stress corrosion problems in the field can be obtained, a basic understanding of the mechanisms and causes of stress corrosion must be obtained. In this light, another more basic research program has been undertaken under our sponsorship. The purpose of this program is to determine the mechanism of stress corrosion cracking in face-centered-cubic metals. In this program ternary iron-nickel-chromium alloy single crystals are being investigated. The stress-corrosion susceptibilities of these austenitic single crystals will be correlated with strain-rate-sensitivity measurements as a function of composition. It is hoped that the strain rate dependency of yielding can be expressed directly in terms of dislocation velocities. The long term problem is to elucidate mechanisms which can give reduced dislocation velocities, and to see whether low velocities correlate with stress corrosion susceptibility.

Ductile Brittle Transition

At elevated temperatures, the usefulness of a material usually is limited either by strength considerations or by oxidation protection problems. However, if the material is used at low temperatures, or is subjected to a multiaxial stress system, it may display a pronounced tendency toward brittle behavior. Usual design criteria cannot predict failure adequately under these conditions. The classic example is the catastrophic failure of Liberty ships during World War II when the calculated stresses were far below usual design limitations. The normally ductile structural steels used in these ships became quite brittle when under the combined effects of low temperatures and multiaxial stress systems. The refractory metals, in fact all body-centered-cubic metals, tend to exhibit this marked decrease in ductility and susceptibility to cleavage fractures at low temperatures. Therefore, the theoretical knowledge gained in the investigation of the brittle failure of steels can profitably be applied to the fracture study of the refractory metals.

One such program which we have (41), utilizes notched and unnotched tensile tests to explore the ductile to brittle transition temperature of the refractory metals tungsten, molybdenum, columbium and tantalum. These metals have been studied in the wrought and recrystallized condition over a total temperature range covering the ductile-brittle transition and are now being studied as a function of interstitial content. From these tests, relations such as are illustrated in figures 13 and 14 can be determined. These figures indicate the very broad temperature range, within which the refractory metals display a transition characteristic. By making strength and ductility measurements, and fracture appearance observations as a function of such variables as temperature, stress concentration factor, strain rate etc. a relatively quick, general and practical definition of ductile to brittle transition can be established.

While the above approach provides a broad view of the transition characteristics of the refractory metals and gives qualitative agreement with fracture mechanics, a more refined and concentrated study is needed to understand the contributions which metallurgical variables are making in the ductile to brittle transition. To do this a more basic approach has been adopted, with dislocation theory providing the basis for the fundamental studies. In these studies Petch (42) and Cottrell (43) models, describing transition behavior, are used to study the various microstructural variables. Investigations, using such models, are being carried out in order to answer such questions as; why tantalum is resistant to brittle fracture while tungsten is not. Continuation of this line of approach should provide some basis for control of brittleness in refractory metals and their alloys.

The strain aging tendencies of columbium are being investigated (44) using yield point return and dynamic modulus measurements to study the aging process, as a function of hydrogen content. Comparison of activation energies for strain aging with those for interstitial diffusion revealed that hydrogen could be responsible for dislocation locking in columbium at low temperatures. The temperature dependence of the yield point and dynamic modulus recovery was found to be adequately expressed by an Arrhenius type rate equation. The activation energies found by the yield point and dynamic modulus recovery techniques bracketed that of 9,370 cal/mol given by Albrecht for diffusion of hydrogen in columbium. In order to obtain a measure of the degree of dislocation locking as a function of hydrogen content, the tensile lower yield stress of columbium was determined as a function of grain diameter using constant strain rate and test temperature. The locking strength, was found to increase with increasing hydrogen content. In further work on columbium the strain rate and temperature dependencies of low temperature deformation behavior of fine grain columbium were investigated. An apparent activation energy of 8300 cal/mol for the early stages of low temperature deformation indicates that stress induced diffusion of hydrogen may be the rate controlling mechanism of the early stages of low temperature deformation of columbium. Increasing the strain rate causes a decrease in the ductile-to-brittle transition temperature of fine grained arc melted columbium, for constant hydrogen content. This decrease in transition temperature may be due to slow strain rate hydrogen embrittlement. Raising the hydrogen content of columbium causes a measurable increase in the ductile-to-brittle transition temperature and also has slight solid solution strengthening effects.

The conclusions of the above work indicate that a hydrogen-dislocation interaction can influence the mechanical behavior of columbium at low temperatures.

Ceramic Materials

A large effort, which is centered around single and polycrystalline Al_2O_3 and MgO , is being devoted to the study of brittle behavior of ceramic materials (45). The program is designed to give consideration to the many factors which contribute to brittle fracture and the mechanisms which can be controlled to introduce plastic behavior. Because of the broad scope of this program only a superficial treatment will be given in order to bring out the salient features of the approach.

The program is broken down into eleven different areas of investigation. Several of these areas will be briefly outlined below:

Static Fatigue: Delayed Fracture

A study is being made of the corrosion processes which may be of importance in controlling the long-term strength of single crystals of Al_2O_3 and MgO , and polycrystalline aggregates of these oxides. It is desired to obtain information on the identity of the corrosion reactions, their mechanisms, and their effect on the rupture strength of these ceramics.

Internal Friction Studies

This study seeks to determine the effect of defects and vacancies upon the fracture dynamics of brittle materials. This aim is to be accomplished by mechanical loss measurements (damping), in order to correlate them with dynamic effects occurring during defect motion.

Effect of Microstructure

The success of current theories by Stroh, Cottrell, Petch, and others dealing with the atomic mechanism of cleavage fracture in metallic lattices has promoted an extension of this thinking to a study of fracture behavior in ceramic materials. This approach is being used to study the deformation behavior of polycrystalline alumina and magnesia. This work will study the influence of grain size on yield and fracture strength over a temperature range covering both ductile and brittle behavior.

Effect of Impurity Content

Work is being directed toward the understanding of the effect of impurities on the mechanical properties of alumina and magnesia. Impurities will be introduced into the polycrystalline alumina and magnesia by two methods: either by adding them to the starting powder, or by diffusing them into the finished specimens from the outer surface. The mechanical properties will then be evaluated as a function of impurity content.

Effects of Structural Size

This area seeks to resolve the problem of the effect of structural size upon the fracture strength of brittle materials. The approach to the solution is based on Weibull's "Statistical Theory of Failure". The work consists of studying the fracture characteristics of two grades of Al_2O_3 and MgO at various temperatures and atmospheric conditions. The statistical failure variability will be obtained from testing identical specimens. The size effects will be observed from experiments using specimens of similar geometrical shape by varying size. The purpose is to obtain an insight into the effects of varying conditions and size on the fracture strength. An attempt will be made to formulate a design equation for service application of brittle materials from the empirical constants determined during the course of this work.

The above abstracts of work in the ceramic area are supplemented by other studies dealing with such subjects as effect of thermal-mechanical history, effect of strain rate, effect of non-uniform stress fields, effect of surface energy, surface active environments, and fracture mechanisms.

Summary

The material presented in the foregoing sections has by no means covered completely the area of mechanical behavior, nor have those aspects treated here been given a full measure of attention. Time and space limitations of course prevent a full treatment. We hope, however, that we have successfully and effectively underlined the point that our advancing aerospace technology has forcibly established and defined imposing performance requirements for materials development and their proper use in present and planned aerospace enterprises. The fact has become quite clear that we can no longer study phenomena singly and out of context and expect a total solution by merely summing the individual effects. It seems imperative to study materials characteristics in their relationship with one another in order to understand their total nature and response to a set of environmental circumstances.

In reviewing areas in which additional work is needed for the future, one could easily generate a list of research without an end. However, from a weapon systems development point of view, we feel there are certain gaps in our knowledge of materials behavior

which warrant particular attention at the moment. Some of these areas are enumerated as follows, although again, we are not all inclusive here:

1. Development of improved observational techniques such as x-ray and electron microscopy, etc., for observations of mechanisms.
2. Additional research on the mechanisms of fatigue and creep geared mainly toward the interpretation of these phenomena in terms of bulk behavior.
3. Research on corrosion-fatigue from a basic electro-chemical and physical viewpoint as opposed to a test data correlation procedure.
4. Expansion of research on spatial and temporal pressure and stress correlations across structural airframes leading ultimately to reliable scaling laws.
5. Additional research on the chemistry of viscoelastic materials aimed specifically at optimum dynamic mechanical properties over broad temperature and frequency bands for energy dissipation purposes.
6. Investigation of viscoelastic materials subjected to thermal gradients with particular reference to the physical properties. Modification and improvement of design procedures under extreme thermal conditions.
7. Development of non-linear viscoelasticity theory with particular emphasis on the stress-strain relations and their application to structural design problems.
8. Research on non-linear theory of elasticity, with reference to shells, and application to stability problems in composite structures.
9. Development of "equivalent damage level" load spectra to simplify random loading problems (this requires both statistical and experimental input).
10. Additional studies of long time temperature and strain effects on structural materials properties.
11. Research on plasticity theory which takes into account the thermal stresses due to non-uniform temperature, fields and improvement of concepts of design to account for thermal stress gradients.
12. Research on aerothermoelastic effects on high speed flight structural components by considering them a combination of aeroelasticity and thermoelasticity.
13. Research on stress-corrosion, directed particularly along fundamental lines, in order to support solutions of problems on sound metallurgical bases rather than apply stop-gap measures such as shotpeening, anodizing, stress-relief or redesign.
14. Research designed to elucidate the influence of microstructural variables on fracture behavior of materials with particular emphasis on understanding the complex fracture problem in engineering materials as compared to pure model materials.
15. Additional research in the general area of the anelastic behavior of materials including delayed yielding, elastic after effects, internal friction, stress-relaxation, etc.

16. Development of new techniques for measuring deformation behavior of metals, including notch root strain rates, high temperature strain, etc.

REFERENCES

1. Broom, T. and Ham, R.K., Proc. Roy. Soc., (1959) A251, p. 186.
2. Grosskreutz, J.C., "Research on the Mechanisms of Fatigue", Air Force Contract AF 33(616)-6383, to be published.
3. Wadsworth, N.J. and Huchings, J., Phil Mag, Vol. 3, p. 1154.
4. Grosskreutz, J.C., "Research on the Mechanisms of Fatigue", WADD TR 60-313, April 1960.
5. Vitovec, F.H. and Lazan, B.J., "Fatigue, Creep and Rupture Properties of Heat Resistant Materials", WADC TR 56-181, August 1956.
6. Dyer, I., Franken, P.A. and E.E. Ungar, "Noise Environments of Flight Vehicles", WADC - University of Minnesota Conference on Acoustical Fatigue, WADC TR 59-676, April 1961.
7. Trapp, W.J. and Lazan, B.J., "Material Properties Which Affect Acoustical Fatigue Life and the Role of Damping", ASTM Spec. Tech. Publ. No. 284, (1960).
8. Fine, M.E., "Dynamic Methods for Determining the Elastic Constants and Their Temperature Variation in Metals", ASTM Special Tech. Publication No. 129, p. 43, June 25, 1952.
9. Zener, C., "Elasticity and Anelasticity of Metals", Univ. of Chicago Press, 1948.
10. Hill, W.H. and Shimmin, K.D., "Elevated Temperature Dynamic Elastic Moduli of Various Metallic Materials", WADD TR 60-438, to be distributed.
11. Hill, W.H. and Wilcox, B.A., "Elevated Temperature Dynamic Moduli of Vanadium, Titanium and V-Ti Alloys", WADD TR 60-245, May 1960.
12. Freudenthal, A.M., Heller, R.A. and O'Leary, P.J., "Cumulative Fatigue Damage of Aircraft Structural Materials: 2024 and 7075 Aluminum Alloy", WADC TR 55-273, Part I, June 1955.
13. Freudenthal, A.M. and R.A. Heller, "Cumulative Fatigue Damage of Aircraft Structural Materials: 2024 and 7075 Aluminum Alloy Additional Data and Evaluation", WADC TR 55-273, Part II, October 1956.
14. Freudenthal, A.M. and Heller, R.A., "On Stress Interaction in Fatigue and a Cumulative Damage Rule: 2024 Aluminum and SAE 4340 Steel Alloys", WADC TR 58-69, Part I, June 1958.

REFERENCES (Cont'd)

15. Freudenthal, A.M. and Heller, R.A., "On Stress Interaction in Fatigue and a Cumulative Damage Rule: 7075 Aluminum Alloy", WADC TR 58-69, Part II, February 1960.
16. Heller, R.A., "Reduction of the Endurance Limit as a Result of Stress Interaction in Fatigue", WADD TR 60-752, May 1961.
17. Weibull, W., "Means of Improving the Efficiency of a Fatigue Test, Proc. WADC - University of Minnesota Conference on Acoustical Fatigue, WADC TR 59-676, April 1960.
18. Weibull, Waloddi, "Statistical Evaluation of Data From Fatigue and Creep-Rupture Tests: Fundamental Concepts and General Methods", WADC TR 59-400, Part I, September 1959.
19. Weibull, Waloddi, "Statistical Evaluation of Data From Fatigue and Creep-Rupture Tests: Efficient Estimation of Weibull Distribution Parameters", WADC TR 59-400, Part II, September 1961.
20. Freudenthal, A.M., "Prediction of Fatigue Life", J. Appl. Phys., Vol. 31, No. 12, 2196-2198, Dec. 1960.
21. Freudenthal, A.M. and Shinozuka, M., "Structural Safety Under Conditions of Ultimate Load Failure and Fatigue", WADD TR 61-177, July, 1961.
22. Sherby, O.D., Lytton, J.L. and Dorn J.E., "Activation Energies for Creep of High Purity Aluminum", Acta Metallurgica, Vol. 5, April, 1957.
23. Dorn, J.E., "Spectrum of Activation Energies for the Creep of Metals", ASM Seminar on Creep and Recovery, p. 255, 1956.
24. Jaffe, N. and Dorn, J.E., "Effect of Temperature on the Creep of Poly-crystalline Aluminum by the Cross-Slip Mechanism", WADD TR 60-53, June 1960.
25. Bayce, A., Ludemann, W.D., Shepard, L.A. and Dorn, J.E., "The Effect of Stress on the Creep Behavior of High Purity Aluminum in the Region of Dislocation Climb, WADC TR 58-507, March 1959.
26. Freudenthal, A.M., "Stress-Relaxation in Structural Materials", WADC TR 58-168, October 1959.
27. Cottrell, A.H. and Ayetkin, V., Journal of the Institute of Metals, Vol. 77, p. 413.
28. Carreker, R.P., Leschen, J.G. and Lubahn, J.D., Trans. AIME, Vol. 180, p. 139 (1949).
29. Corten, H.T., Clark, M.E. and Sidebottom, O.M., Journal of Appl. Mech., Paper 51-F-4, (1951).
30. Albrecht, B., Bieniek, M. and Freudenthal, A.M., "Stress-Relaxation in Structural Metals at Elevated Temperatures", Contract AF 33(616)-6112, to be published.

REFERENCES (Cont'd)

31. Ebcioglu, I.K., "Thermo-Elastic Equations for a Sandwich Panel Under Arbitrary Temperature Distribution, Transverse Load and Edge Compression, ASD TR 61-128, to be distributed.
32. Reissner, E., "Finite Deflections of Sandwich Plates", J. Aero Sciences, pp. 435-440, July 1948.
33. Hoff, N.J., "Bending and Buckling of Rectangular Sandwich Plates", NACA TN 2225, November 1950.
34. Chang, C.C. and Ebcioglu, I.K., "Thermo-Elastic Behavior of Simply Supported Sandwich Panel Under Large Temperature Gradient and Edge Compression", Publication by J. Aero/Space Sciences, Vol. 28, No. 6, pp. 480-492, June 1961.
35. Papirno, Ralph and Gerard, George, "Investigation of Creep Buckling of Columns of 2024-0 Aluminum Alloy", WADC TR 59-416, Part III, June 1961.
36. Gerard, G., "A Creep Buckling Hypothesis", J. Aero. Sci., Vol. 23, No. 9, Sept. 1956, pp. 879-883.
37. Griffith, A.A., "Phenomena of Rupture and Flow in Solids", Phil. Trans. Roy. Soc. (London), Vol. 221, Series A, (1920).
38. Irwin, G.R. and Kies, J.A., "Fracture Theory as Applied to High-Strength Steels for Pressure Vessels, Golden Gate Metals Conference, San Francisco, (1960).
39. Weiss, V., Sessler, J.G. Packman, P. and Sach, G., "The Effect of Several Geometrical Variables on the Notch Tensile Strength of 4340 Steel Sheet Heat Treated to Three Strength Levels", WADD TR 60-310, September 1960.
40. Crossley, F.A., Reichel, C.J., Simcoe, C.R., "The Determination of the Effects of Elevated Temperature on the Stress Corrosion Behavior of Structural Materials", WADD TR 60-191, May 1960.
41. Ingram, A.G., Holden, F.C., Ogden, H.R., Jaffee, R.I., "Notch Sensitivity of Refractory Metals", WADD TR 60-278, September 1960.
42. Petch, N.J., J. Iron Steel Inst., 1953, Vol. 173, p. 25.
43. Cottrell, A.H., Trans. AIME, 1958, Vol. 212, No. 2, p. 192.
44. Wilcox, B.A., Huggins, R.A., "Effect of Hydrogen on Dislocation Locking in Niobium", J. of the Less-Common Metals, 1960, Vol. 2, No. 2-4, p. 292.
45. Weill, N.A., "Studies of the Brittle Behavior of Ceramic Materials", ARF 8203-6, Semi-Annual Report, 1960, Contract No. AF 33(616)-7465.

STRESS RANGE DIAGRAM FOR 6.3% Mo - WASPALLOY at 1500°F

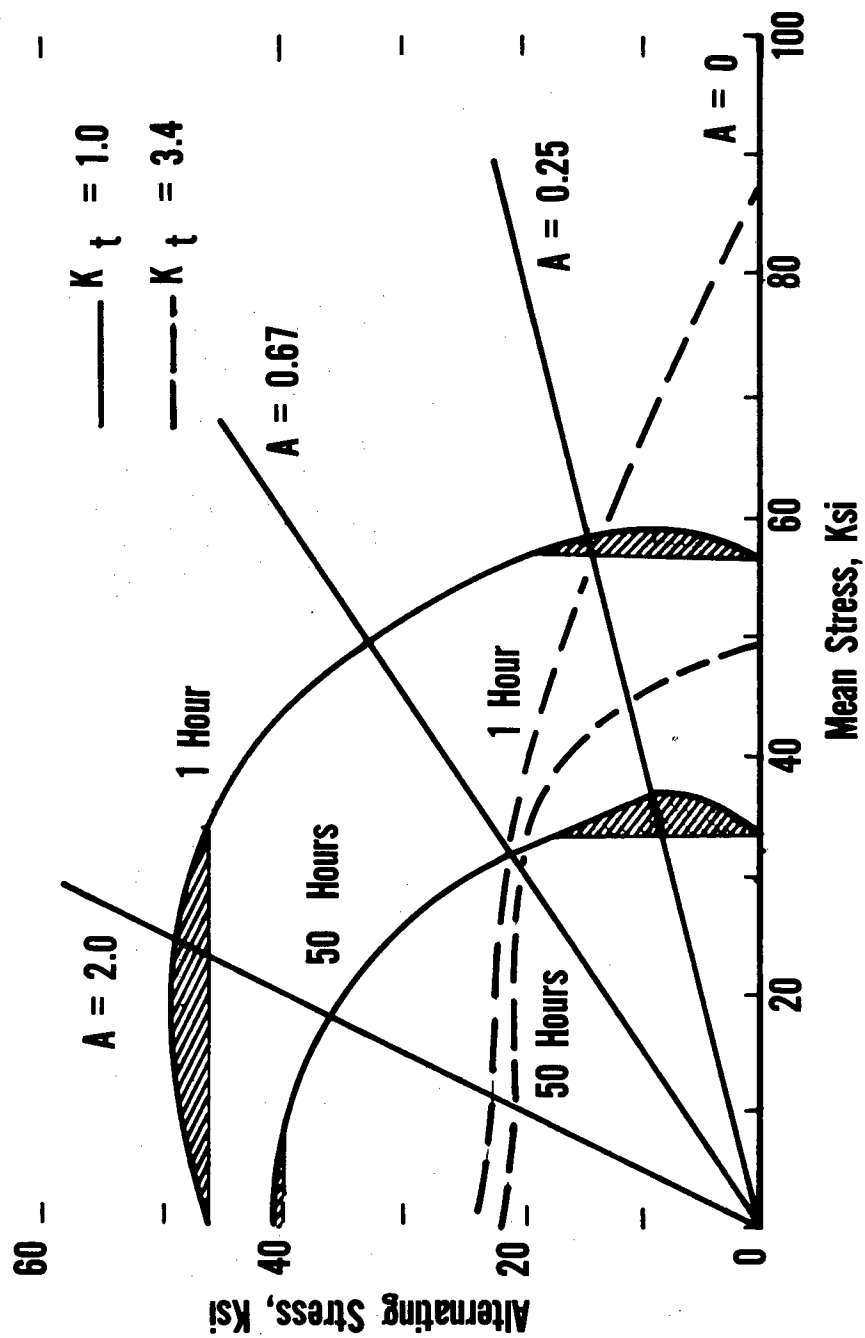


Figure 1.

ACOUSTICAL FATIGUE FAILURES

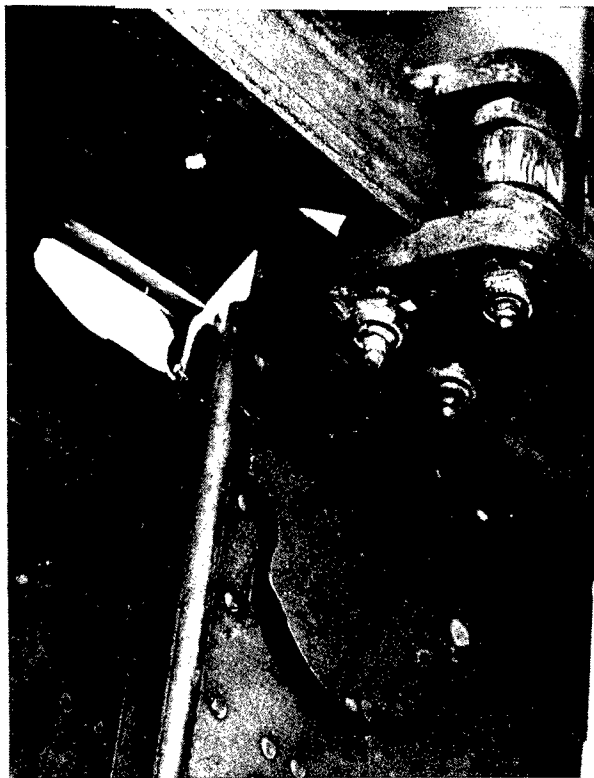


Figure 2.

TYPICAL SOUND PRESSURE - FREQUENCY SPECTRA

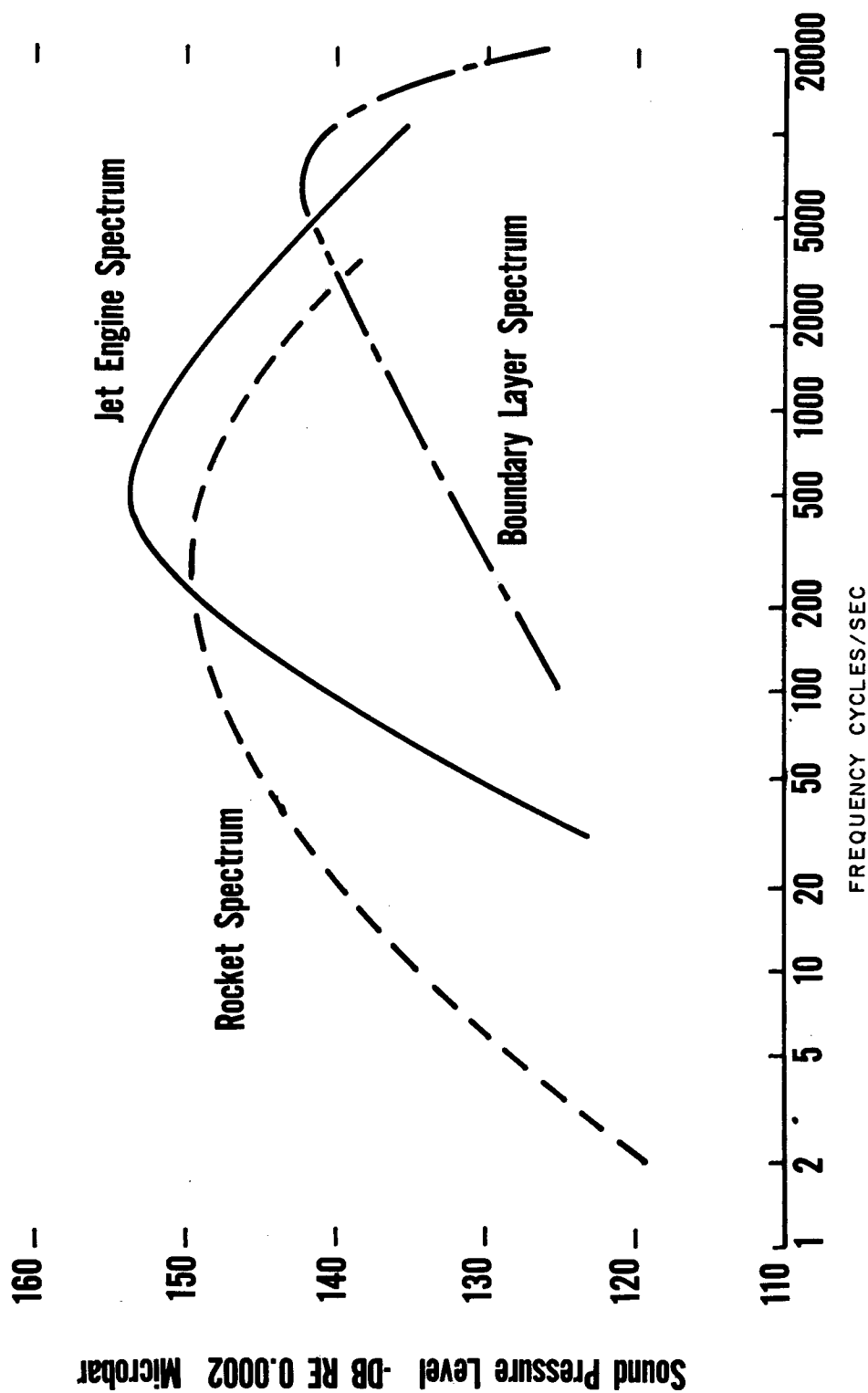


Figure 3.

ACOUSTIC POWER LEVELS FOR F-100 AIRCRAFT IN FLIGHT

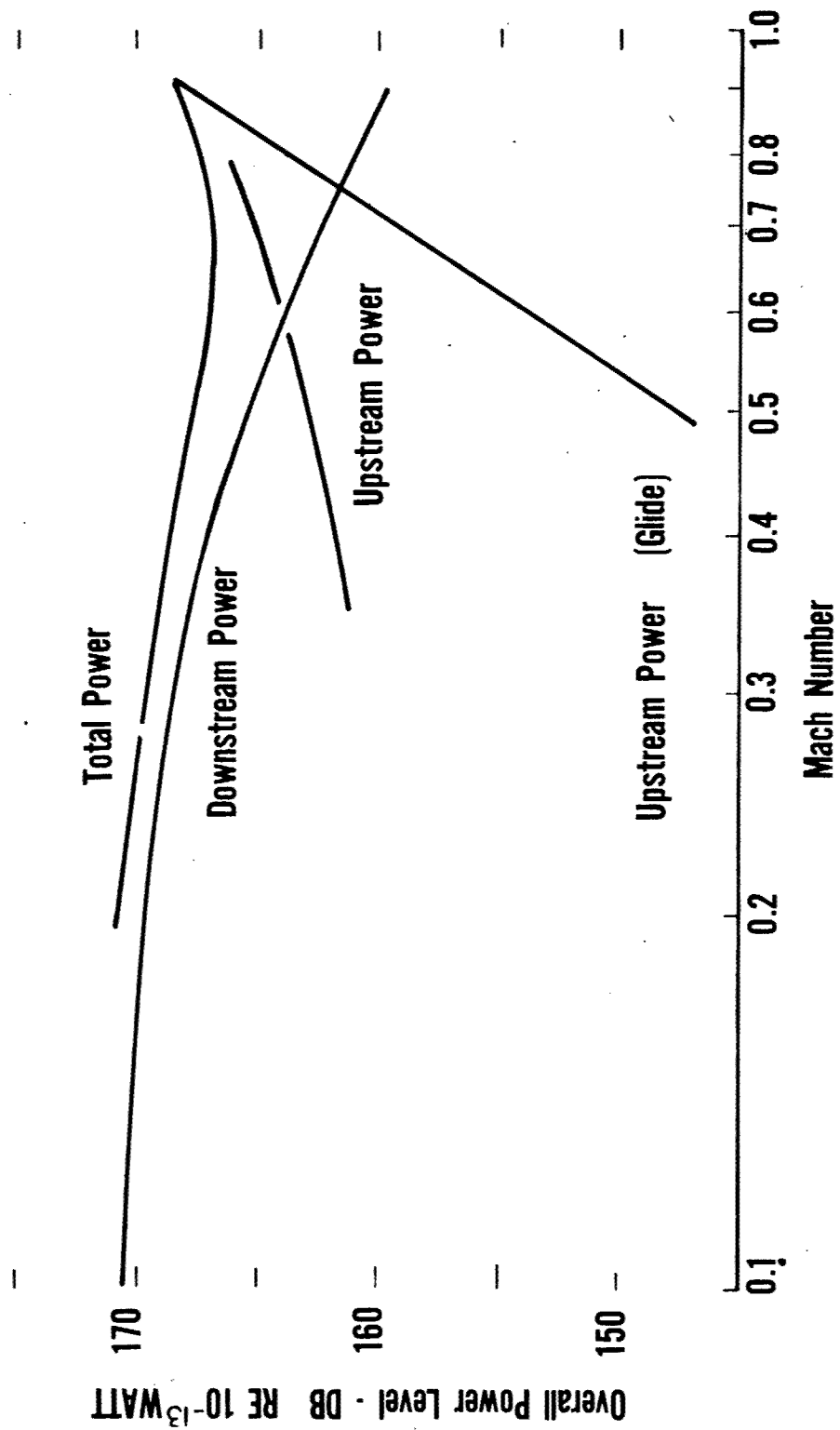


Figure 4.

EXAMPLES OF CONFIGURATIONAL DAMPING

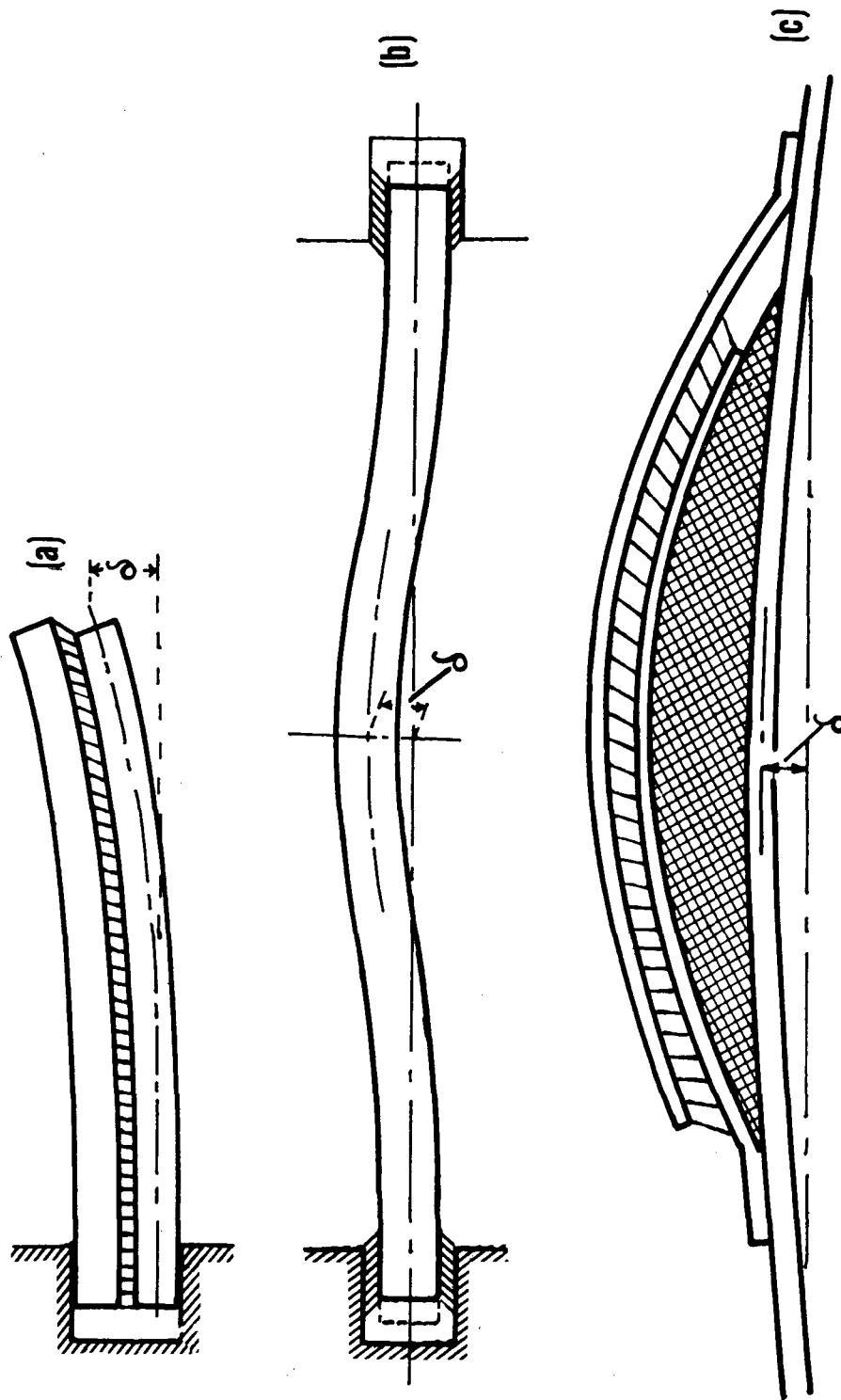


Figure 5.

DYNAMIC MODULUS OF ELASTICITY v.s. Temperature

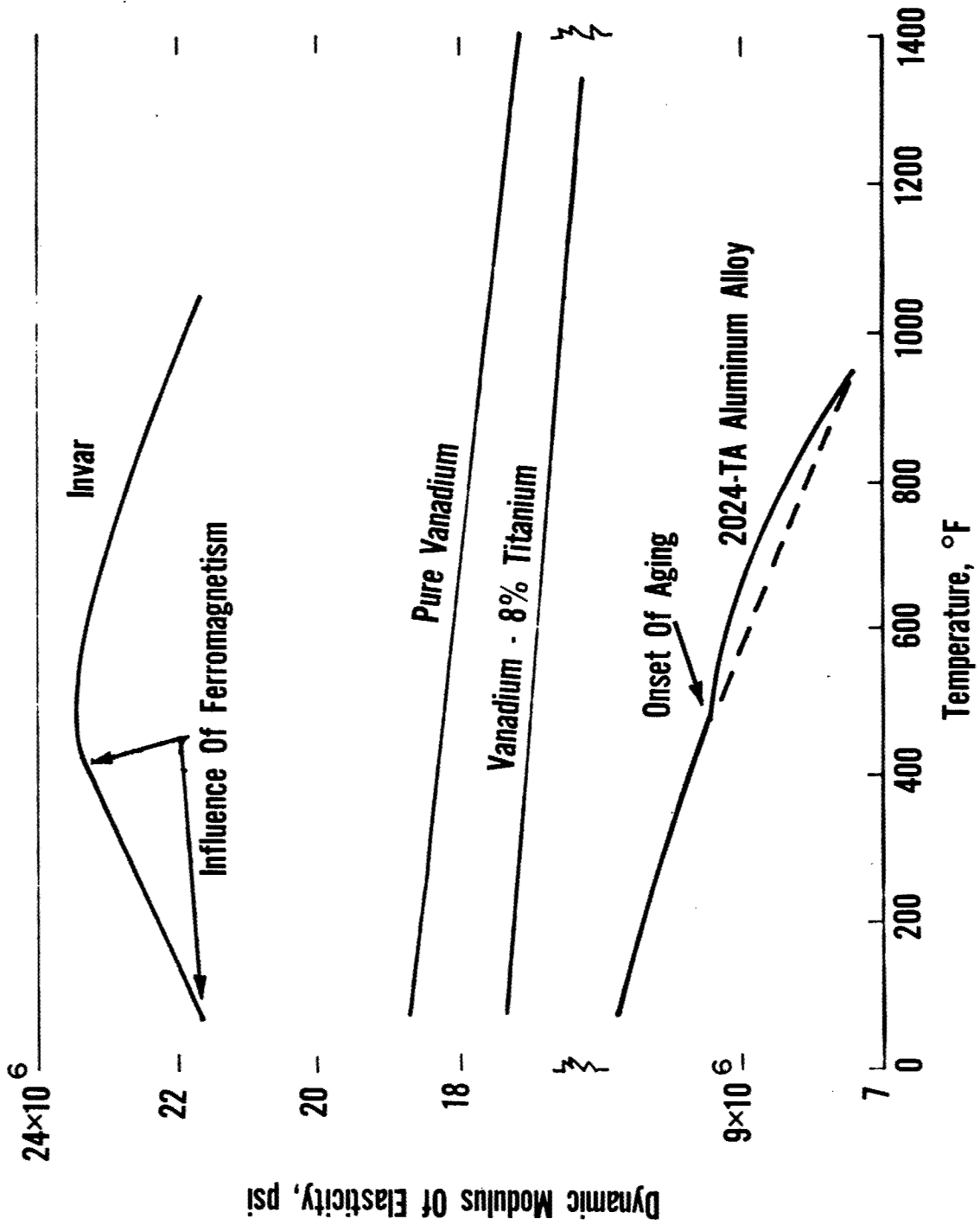


Figure 6.

TRUE RANDOM FATIGUE LIFE AS FUNCTION OF LINEAR LIFE

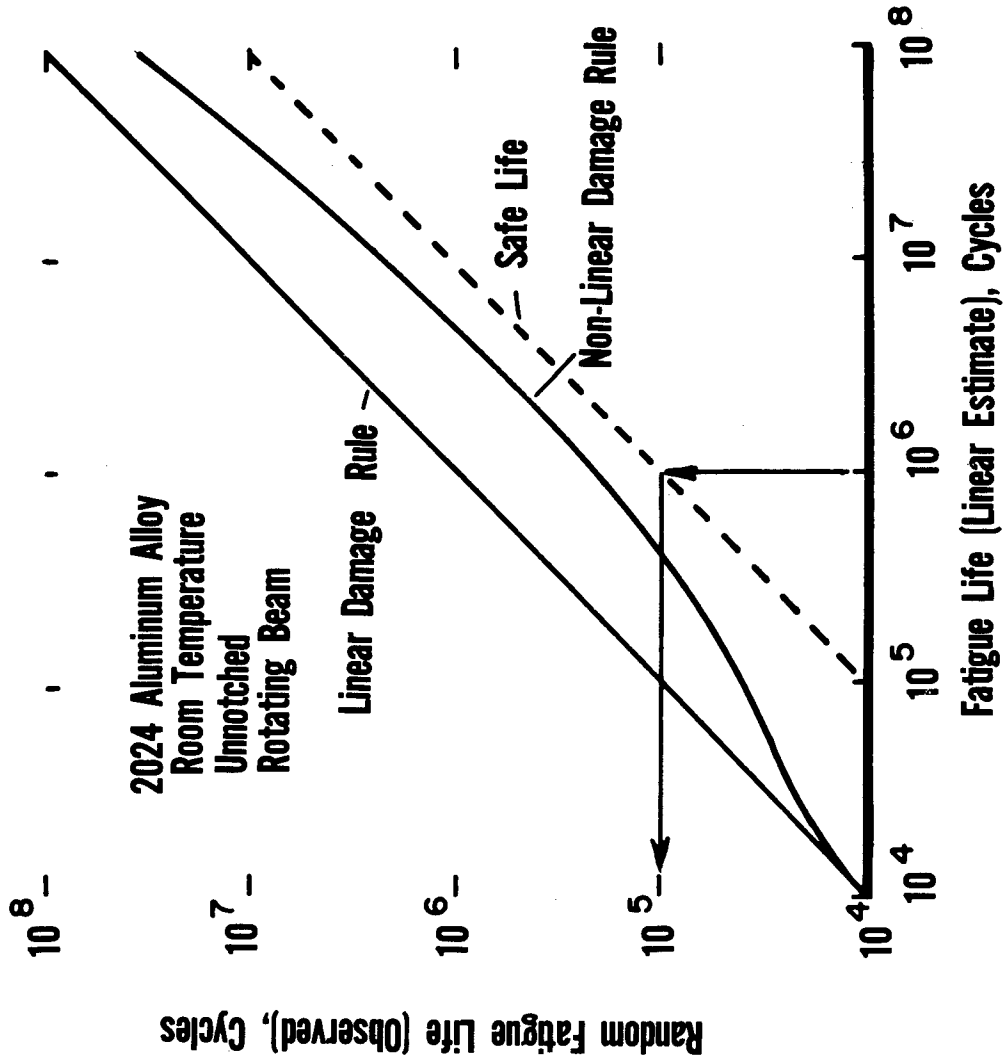


Figure 7.

ACTIVATION ENERGIES v.s. TEMPERATURE FOR PURE ALUMINUM

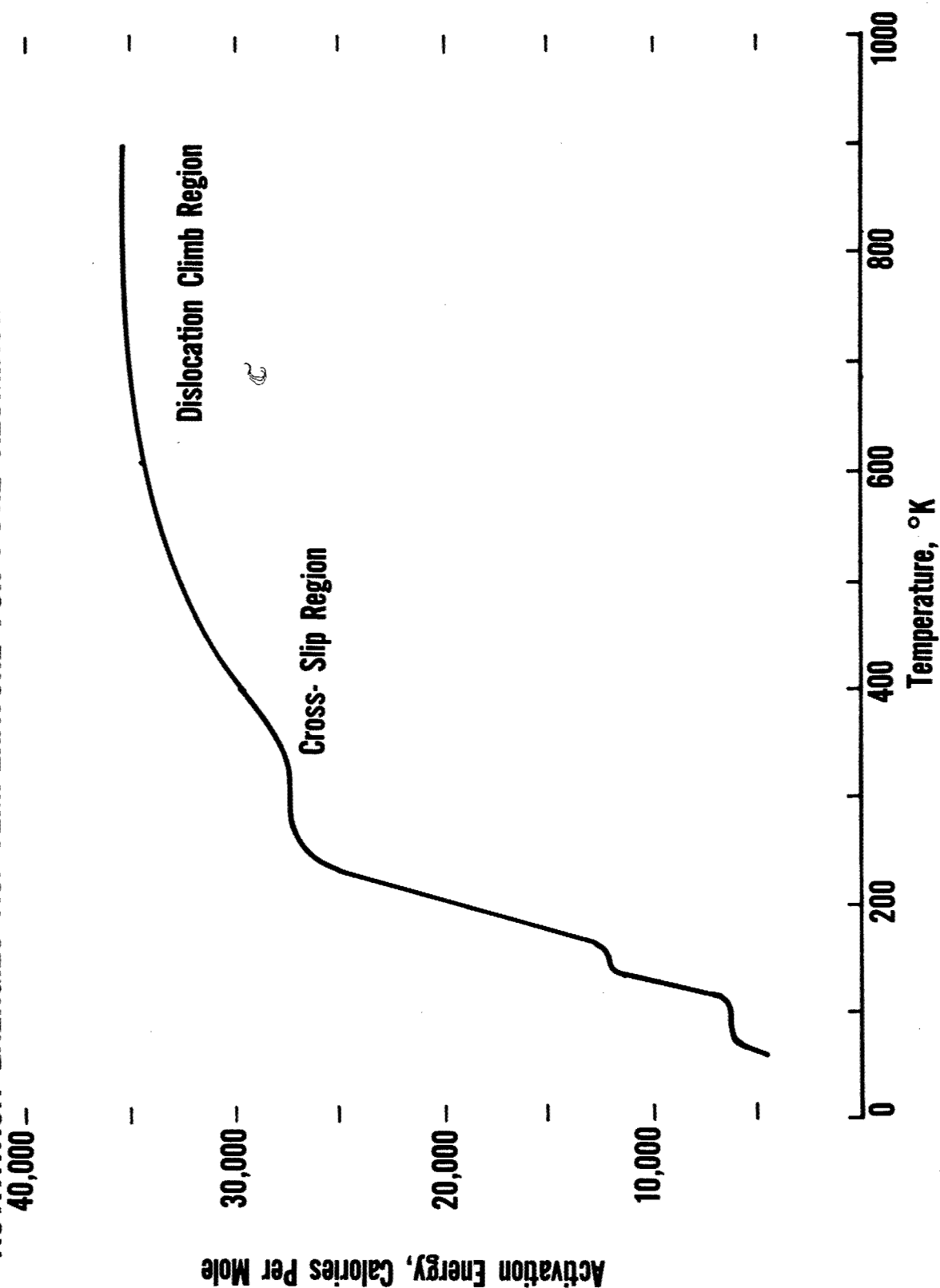


Figure 8.

STRAIN - TIME CURVES FOR 2024 - T 4 ALUMINUM

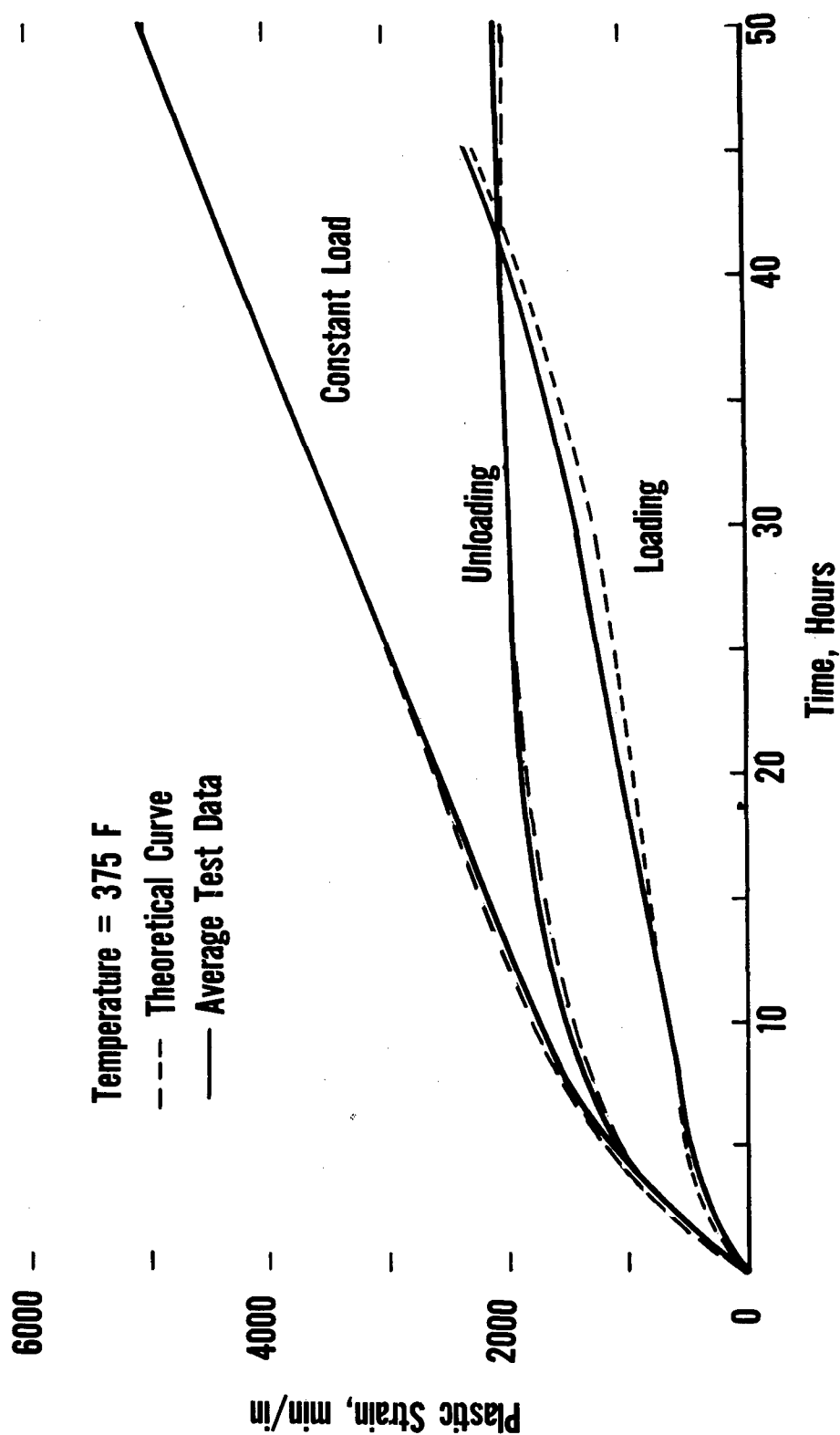


Figure 9.

DIFFERENTIAL EQUATIONS

$$\frac{(1+m)E\hat{t}}{2m(1-\mu^2)} [2\bar{u}_{,xx} + (1-\mu)\bar{u}_{,yy} + (1+\mu)\bar{v}_{,xy}] = \frac{1}{1-\mu} (E\hat{t}\alpha' T' + E\hat{t}\alpha'' T''),_{x}$$

$$\frac{(1+m)E\hat{t}}{2m(1-\mu^2)} [2\bar{v}_{,xy} + (1-\mu)\bar{v}_{,xx} + (1+\mu)\bar{u}_{,xy}] = \frac{1}{1-\mu} (E\hat{t}\alpha' T' + E\hat{t}\alpha'' T''),_{y}$$

$$\frac{(1+m)E\hat{t}}{2m(1-\mu^2)} [2u_{,xx} + (1-\mu)u_{,yy} + (1+\mu)v_{,xy}] - \frac{1+m}{\hat{t}} \bar{H}_x \left(\frac{1+m}{m\hat{t}} u + \hat{t} w_{,x} \right) = \frac{E\hat{t}}{1-\mu} (\alpha' T' - \alpha'' T''),_{x}$$

$$\frac{(1+m)E\hat{t}}{2m(1-\mu^2)} [2v_{,xy} + (1-\mu)v_{,xx} + (1+\mu)u_{,xy}] - \frac{1+m}{\hat{t}} \bar{H}_y \left(\frac{1+m}{m\hat{t}} v + \hat{t} w_{,y} \right) = \frac{E\hat{t}}{1-\mu} (\alpha' T' - \alpha'' T''),_{y}$$

$$- \frac{E\hat{t}^{1/3} + E\hat{t}^{1/3}}{12(1-\mu^2)} \nabla^4 w + \hat{t} \bar{H}_x \left(\frac{1+m}{m\hat{t}} u_{,x} + \hat{t} w_{,xx} \right) + \hat{t} \bar{H}_y \left(\frac{1+m}{m\hat{t}} v_{,y} + \hat{t} w_{,yy} \right) + N_{xx} w_{,xx} + 2N_{xy} w_{,xy} + N_{yy} w_{,yy} + q + q'' = \nabla^2 (M' + \dot{M})$$

Figure 10.

NOTCH STRENGTH V.S. STRESS GRADIENT

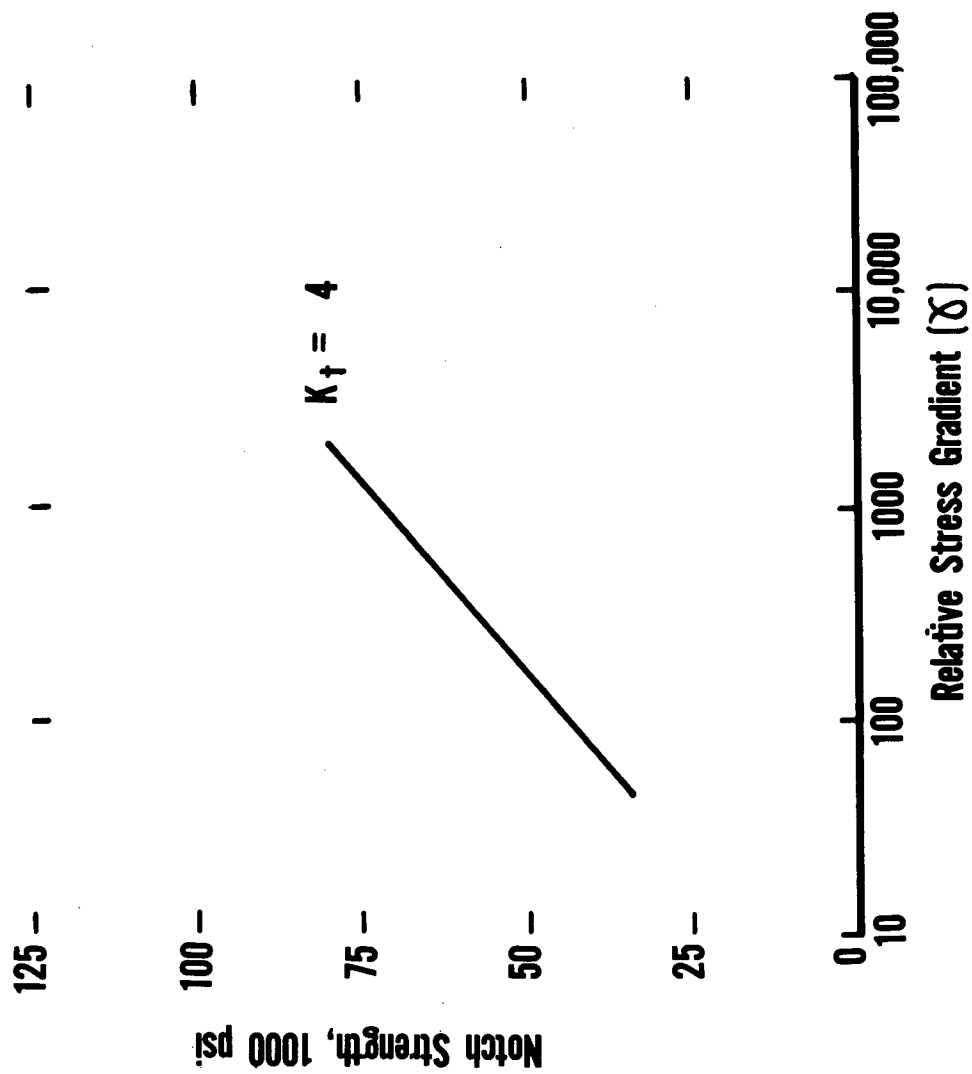


Figure 11.

NOTCH STRENGTH V.S. NOTCH DEPTH

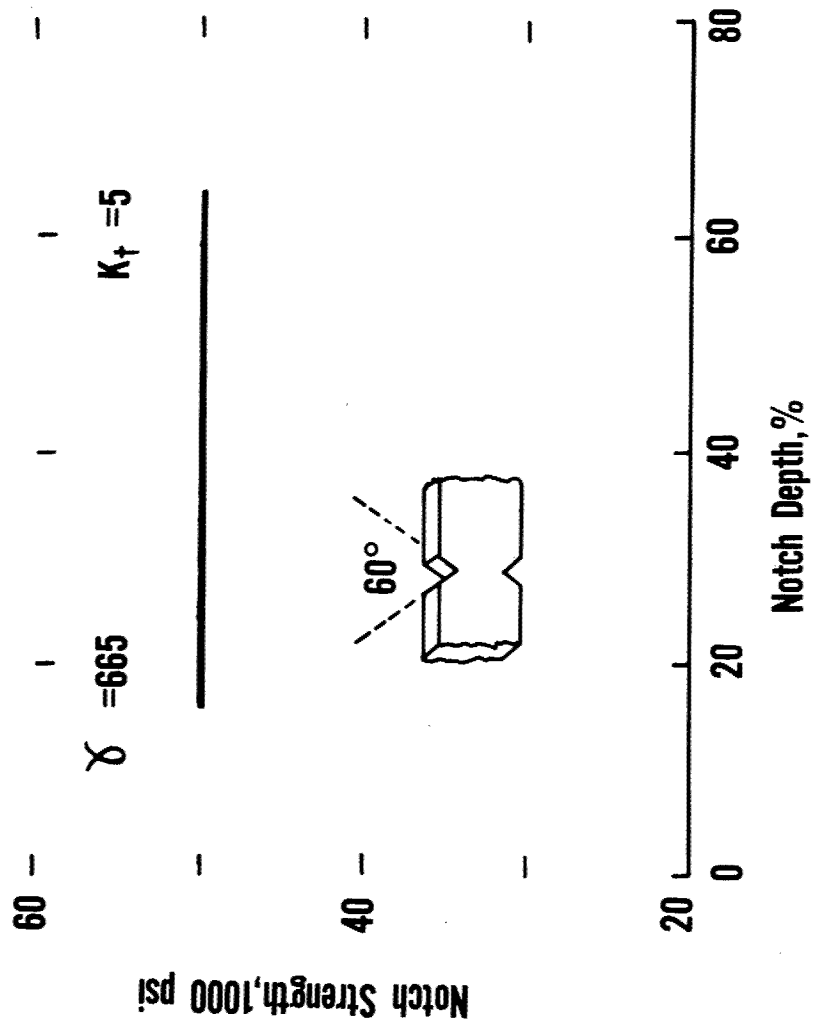


Figure 12.

NOTCH-UNNOTCH STRENGTH RATIOS FOR THE RECRYSTALLIZED MATERIALS

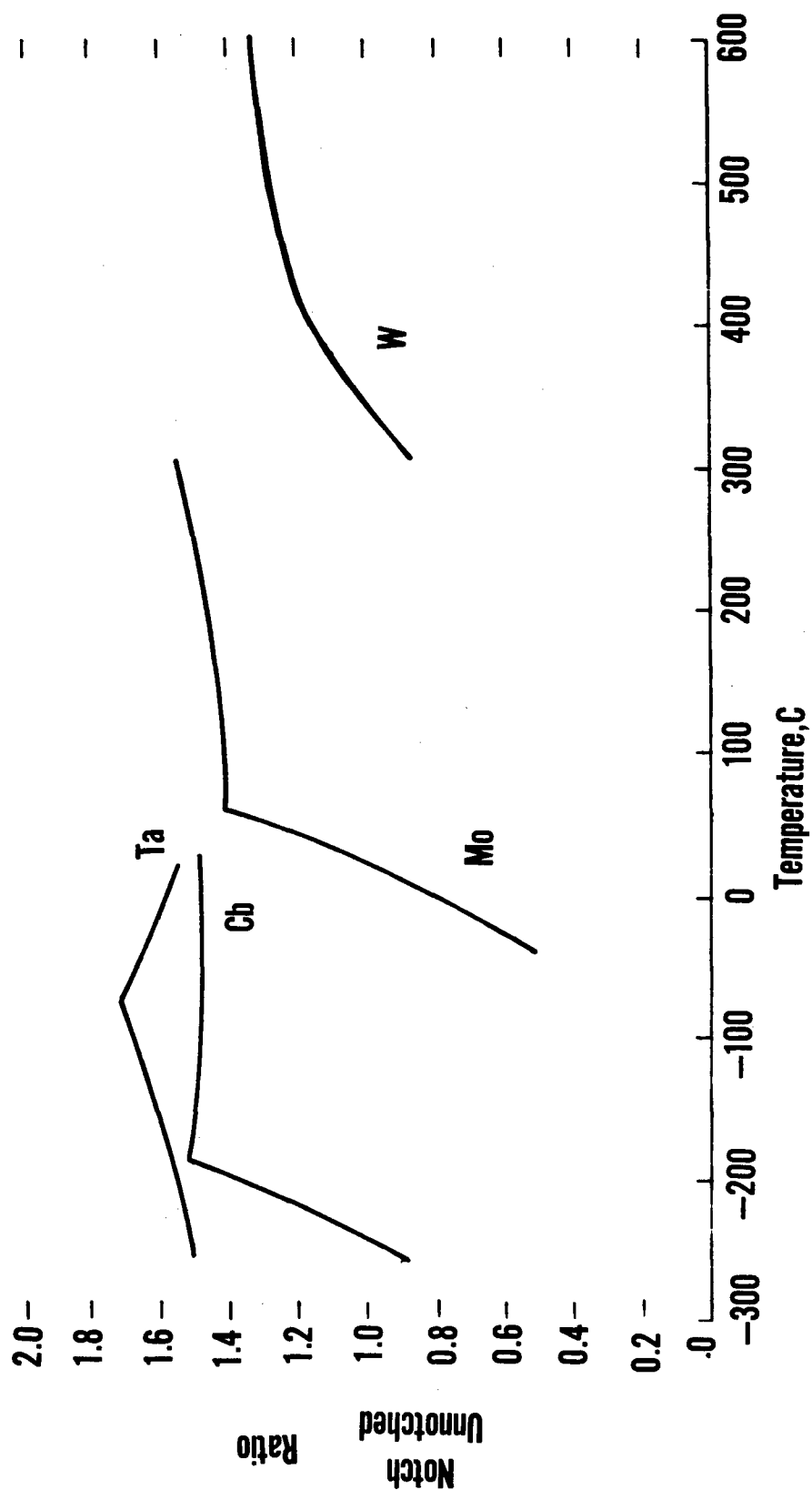


Figure 13.

DUCTILITY FOR RECRYSTALLIZED MATERIAL

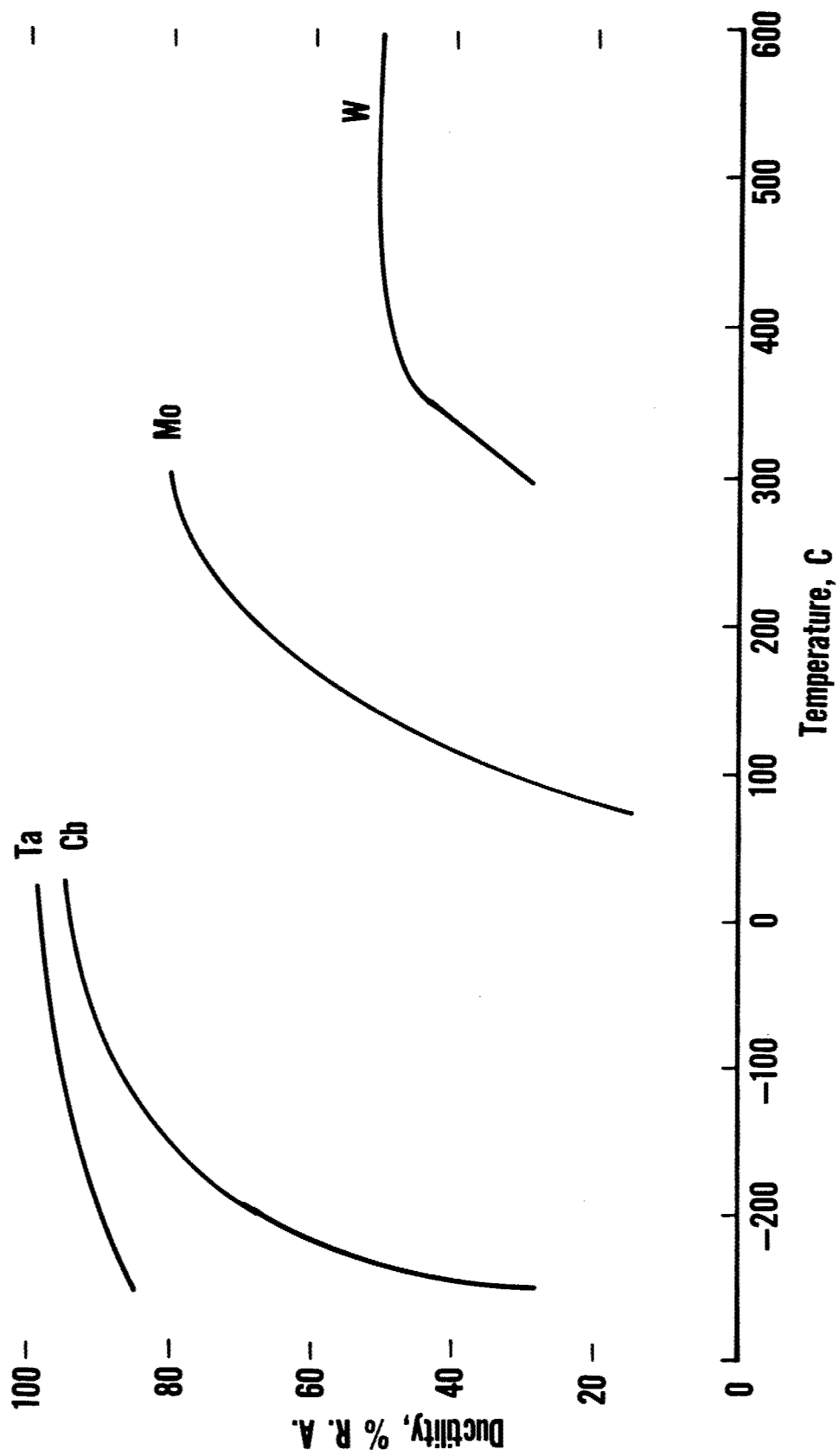


Figure 14.

BERYLLIUM, ITS POTENTIALS AND PROBLEMS

Chairman

Mr. I. Perlmutter

Speaker

Lt S. S. Christopher

Panel Members

Mr. H. Black

Mr. R. Geyton

BERYLLIUM RESEARCH AND DEVELOPMENT

Lt S.S. Christopher

Directorate of Materials and Processes, ASD

Introduction

In reviewing the technology of beryllium that has been generated over the past three years, since the last Air Force Materials Symposium, we find that there has been significant advancement in the four areas of: (1) brittleness (2) joining (3) fabrication of wrought products, and (4) evaluation of the structural integrity of beryllium.

Before we discuss in detail the areas mentioned above, it is important that we review briefly the properties of beryllium that make it attractive to the Air Force as a structural material. The modulus to density ratio of beryllium surpasses that of any other metallic material and this combined with its heat capacity, thermal conductivity, dimensional stability, and relatively high melting point make the metal a necessity for future space systems. No other material has this unique combination of properties to offer design engineers.

Along with the many advantageous properties of beryllium, we find that there are many factors preventing the widespread utilization of the metal. These can be readily summarized as follows: (1) brittleness; (2) joining; (3) preferred orientation in wrought products; (4) casting; and (5) toxicity. It might be well to mention that although the toxicity problem is real, techniques and procedures have been established to the extent that almost any metallurgical process can be applied to beryllium without any harmful effects on personnel.

In view of the great potential of the metal, numerous programs have been initiated by the Air Force, Navy, and the Atomic Energy Commission. These organizations, although having different end items in mind, find that the problems associated with beryllium are basic to all three.

Listed below are specific problems investigated in Air Force beryllium programs, which will be discussed. The problems will be reviewed also as they affect the research and development programs by the other Government agencies mentioned.

BRITTLENESS	JOINING	PROCESSES AND WROUGHT PRODUCTS	STRUCTURAL INTEGRITY
Distillation	Fusion Welding	Rolling	Box Beam
Iodide Decomposition	Resistance Butt Welding	Forging	Thermantic Panels
Aging and Strain Aging	Ultrasonic Welding	Extrusion	Design Handbook
Dislocations	Resistance Spot Welding	Casting	
Splat Cooling	Brazing	Roll Forming	
Oxide Distribution			
Surface Effects			
Increasing Yield Strength			

Brittleness

Brittleness is the predominant factor restricting extended use of beryllium as a structural material. Although many theories have been postulated as to the probable cause of this brittleness, none have been substantiated. However, progress is being made through Government sponsored research and development, coupled with a genuine industrial interest in sustaining an attack on this and related problems.

One of the postulations advanced is that impurities play the major role in causing brittleness in beryllium. Investigations of the past year seem to support this theory. Purification studies have been initiated and three different approaches are being employed: zone refining, distillation, and iodide decomposition.

Zone refining studies under Navy sponsorship at the Franklin Institute (1) have produced beryllium single crystals with ductilities never before attainable. The mechanical property data obtained on these crystals are shown in table 1.

Polycrystalline beryllium being produced by distillation has given purity never before attainable in the metal.* Table 2 is an example of the purity obtained by this technique as compared with Pechiney beryllium. A complete mechanical property evaluation on polycrystalline distilled beryllium will be completed in the near future.

Although beryllium iodide decomposition has not been successful in producing quantities of beryllium sufficient for X-ray or chemical analysis, much has been learned concerning the preparation of pure beryllium iodide, reaction materials, and kinetics of the decomposition. A series of experiments are now under way using a static system in a beryllium reaction chamber. The variables being studied are the temperature gradient between the reaction bulb and the hot filament, concentration of I_2 , and the geometry of the reaction chamber.

Other programs under investigation which tend to support the purification theory are aging and yield point phenomena and dislocation studies in beryllium. Beryllium, solution treated and aged at various temperatures, shows a wide variance in the tensile properties and also the occurrence of a strong yield point. Strain aging studies have given a rough value for the activation energy for return of the yield point and this value is around 50 kilo cal/gm mole. This value is high and it would be expected that a substitutional element was causing this phenomenon.

Wilsdorf (2) strengthens the work of Gelles (2,3) above through actual observation of impurity clusters by electron transmission microscopy. These clusters observed in annealed Pechiney beryllium seem to preferentially precipitate along subgrain boundaries and dislocations (figure 1). This investigation is the first reported direct observation of these precipitates.

Electron transmission techniques (2) are being applied to study the distribution of oxide in hot pressed and wrought beryllium. Replica techniques have been developed and surface-oxidized vacuum melted Pechiney flake is being employed as the starting material to study the oxide films. No conclusive results on this program are available.

* No analysis is available as yet on Franklin Institute zone refined bars.

Other Brittleness Investigations

Surface defects such as cracks and twinning are being evaluated according to the role they play in crack initiation and propagation in beryllium sheet. Metallographic examination of hot pressed sheet in the as-received condition has shown cracks to depths of 0.005 inch and twins to a depth of 0.01 inch. Surface and annealing treatments are being exploited in an attempt to remove the surface imperfections.

Although very little alloy development on beryllium is being supported by the Air Force, a program (2) was initiated to increase the yield strength of beryllium sheet using two approaches: by varying conditions of fabrication and by alloying with copper. The results of this investigation are shown in tables 3 and 4. In comparing this data, we find that copper is a potent strengthening agent, a one percent addition, increases the yield strength from 20 to 50 percent.

Joining

Another problem area in the development of beryllium as a structural material is joining. Fabrication of structural components involves the joining of beryllium to other materials as well as to itself.

Fusion welding (2) of beryllium has resulted in crack free welds in sections under 1/4-inch thick using Metal-arc Inert Gas (MIG) and Tungsten-arc Inert Gas (TIG) processes. Mechanical properties of the welds produced are lower than the properties of the parent metal and techniques such as roll planishing to impart strength to the welds are now being attempted with some success. The primary problems in fusion welding are: (1) poor penetration due to the high heat conductivity of beryllium; (2) excessive grain growth in the weld and heat affected area; (3) development of appropriate filler material; and (4) fixturing.

Resistance butt welding studies are being performed on beryllium 5/8-inch diameter rod. Although welds have been made, sufficient data are not available to evaluate this process.

Ultrasonic welding (2) of beryllium sheet ranging in thickness from 0.010 to 0.013 inch is being attempted. Beryllium to beryllium welds have been made (figure 2), and it should be noted that the grain size in the weld area is not greatly affected by this technique. The limiting factor in this process seems to be the power requirements of the equipment available. To permit joining at a somewhat reduced power setting, interleaf materials are being selected and utilized. The interleaf materials under investigation are molybdenum, zirconium, titanium, gold, and aluminum. A complete analysis of this technique as applied to beryllium is not yet available but the process shows definite promise.

Resistance spot welding (2), now under investigation, consists of making single spot welds on 1 x 1 inch coupons of beryllium at various welding currents while holding all other variables constant. This procedure is repeated for each group of welds made except that one of the variables is changed for each group. This program is in its infancy and no data is now available.

To date, the most reliable method of joining beryllium is considered to be brazing. Silver braze alloys have been developed which give a satisfactory bond with approximately 60 percent of the base metal strength at room temperature.

Fabrication

The fabrication of beryllium into reliable wrought forms such as sheet, forgings, and extrusions has been actively pursued by the Air Force. Fabrication and processing techniques are of the utmost importance in the adaptation of any material to structural usage. Since the primary utilization of a wrought product is in the form of sheet, let us discuss the current state of the art in beryllium sheet rolling (4).

Techniques have been developed for rolling sheet in sizes 24 in. x 60 in. x .020 in. to .060 in. Blended beryllium powder QMV vacuum hot pressed minus 200 mesh is considered the optimum starting material. The hot pressed block is jacketed in mild steel and bidirectionally rolled between 1400 and 1500°F. Bidirectional or cross-rolled beryllium has mechanical properties in the plane of the sheet within 10 percent of each other, generally the highest strength values are obtained in the final or predominant rolling direction. Table 5 is a statistical analysis of the yield strength and elongation of the sheet produced under the various phases of the rolling program. However, the problem now emerges of the ever-present problem of poor, essentially nonexistent, ductility in the short transverse (thickness) direction of the beryllium sheet material. Although the elongation in the plane of the sheet is sufficient for most structural components, utilization is highly limited due to the inability of the sheet material to withstand biaxial stresses. This is attributed to crystallographic orientation, and one must be familiar with the active modes of deformation in beryllium to understand the effect of orientation on anisotropy.

It would be of considerable value at this point to discuss briefly the attempts made to solve the preferred orientation problem. The objectives of these investigations were to obtain a randomly oriented material and evaluate the effect of random orientation on mechanical properties. However, our need is not only one for which a process or technique must prove successful, but one that could be conveniently adapted to large production capability. The first technique tried can be termed "hot-upsetting", wherein an effect comparable to infinite-directional rolling could conceivably be attained (5). Sheet was produced by pure compression applied along the longitudinal axis of a cylindrical beryllium billet machined out of a hot-pressed block. Crystallographic orientation in sheet produced thusly has the basal plane (0001) essentially parallel to the plane of the sheet and the secondary prism plane (11 $\bar{2}$ 0) perpendicular but random with respect to any given direction within the plane of the sheet. The short transverse or third dimensional ductility increases from 0.017 through 0.226 percent (in a bidirectionally rolled) to 1.5 through 2.0 percent (in hot-upset) sheet. The strength and elongation in the plane of the hot-upset sheet are lower, as would be expected.

The second approach to the preferred orientation problem was to obtain random orientation through heat treatment (6). Bidirectionally rolled sheet was annealed at various temperatures ranging from 950° to 1200°C for periods of 0.1 to 10 hours at each temperature. The effects of these various annealing cycles on texture and on third dimensional ductility were measured. X-ray analysis was used to establish pole figures to determine basal plane orientation in the annealed sheet. These figures reveal a basal plane shift of approximately 10 degrees from the plane of the sheet. This drop in basal plane pole population perpendicular to the sheet means that the generally parallel basal plane orientation has been disrupted or has become somewhat randomized. The effect of the high temperature annealing on the basal plane (0001) orientation of bidirectionally rolled sheet is shown in figure 3.

The accompanying increase in third dimensional ductility through high temperature annealing compares favorably with that realized by hot-upsetting. Biaxial ductilities ob-

tained through annealing vary between 1.0 and 1.77 percent with the optimum annealing cycle indication of 1050°C for 0.1 hour.

From this discussion it immediately becomes apparent that although both hot-upsetting and high temperature annealing seem to alleviate the preferred orientation problem, the latter is more conventional and appealing. We can foresee the difficulty which arises with respect to sheet size limitations in the hot-upsetting technique. However, the information obtained through this investigation is extremely valuable. Investigation in a new AMC sheet rolling program will utilize the above information, and provisions are being made for the adaptation of the annealing technique developed. A thorough and comprehensive evaluation of this added feature is programmed.

Evaluation of Structural Integrity

To determine the structural integrity of the bidirectionally rolled sheet produced, many programs have been designed to fabricate and test structural components. These programs have been initiated on theoretical formability, mechanical and physical property evaluation, crack propagation studies, design criteria, coatings, high energy forming processes, etc. Bidirectionally rolled sheet has been supplied to many aircraft companies and research organizations for evaluation under these programs. An example (7) of some of the aforementioned forming and testing that is being accomplished is shown in figure 4.

Results reported from these investigations are as yet very limited and conclusions cannot be drawn. One of the most comprehensive investigations on structural evaluation is in process at the Martin Company (8). The objectives are: to establish a standard measure of merit for characterizing so-called structural beryllium and to determine experimentally the relative superiority of beryllium, in the structural sense. An evaluation is being conducted utilizing hot-upset, hot-pressed, and hot-pressed bidirectionally rolled sheet. Mechanical property evaluation will involve bend tests, notched and smooth tensile tests, bulge tests, compression, and box beam structure testing. Specimens of varying widths and gauge thickness will be used in the bend ductility testing.

Although the evaluation is not complete, considerable progress has been made. Box beams have been fabricated from all three sheet materials and tested by constant moment bending until fracture. The beam and fracture data are shown in figure 5. The designations are: bidirectionally rolled, hot-pressed and hot-upset. Until all the evaluations are complete and the data compiled and correlated with tests and materials, we cannot draw any concrete conclusions concerning the structural merit of beryllium sheet.

Future Recommendations in Beryllium Research and Development

Even with the brief review presented herein, we can readily see that many areas of beryllium research and development necessitate further investigative effort. In addition to problems discussed, attention must also be given to the compilation of design data and, ultimately, testing of structural components for actual use in specified systems. Although, the most promising developments concerned with ductility are centered around purification, further evaluation for conclusive proof that this is the answer and that reproducibility is assured must be accomplished. Results on the single crystal work must be confirmed and the feasibility of zone refining must be substantiated by similar results on polycrystalline material. Once these are resolved and the cause of impurities is isolated, concentrated effort may be expended on developing techniques for producing the degree of purity needed on a commercial scale.

Proven success in the above programs would precipitate further efforts such as study of deformation modes and characteristics, recrystallization and grain growth behavior, alloying characteristics, further development of joining methods, and evaluation of physical and mechanical properties of the high purity material.

If the above course is pursued, another aspect for consideration is the possibility of limited improvement or negative results through purification of beryllium. This would, in effect, dictate the need for a critical review of the basic research effort, and the initiation of new programs designed to answer questions of a more developmental nature. These programs would include studies on the effect of BeO content and distribution on the mechanical properties, aging studies to determine the cause of certain phenomena under certain conditions of time, temperature, and work, and dislocation studies because of the very nature of the data they produce. Results from all these investigations will have to be evaluated and correlated with the specific properties each imparts on the material.

The future of beryllium research and development hinges on a relatively few highly oriented studies currently under way. Yet, great strides have been made, and even more encouraging is the fact that each day more and more people connected with the research and development effort in beryllium are becoming more consistent in their reasoning and in their approaches to the existing problems.

REFERENCES

1. Herman, M., Spangler, G. E., and Hein, E., "The Preparation of High Purity Beryllium and the Study of Its Flow and Fracture Properties," Final Report on Contract NOas 59, 6242-c, June 30, 1959 to June 30, 1960.
2. "Beryllium Research and Development Program," Nuclear Metals, Inc., Contract AF 33(616)-7065.
3. Gelles, S. H., Pickett, J. J., and Wolff, A., "Some Recent Advances in Beryllium Metallurgy," Nuclear Metals, Inc., TJ-31, August 31, 1960.
4. Wikle, K.G., Armstrong, J. W., and Perrin, H. N., "Development of Beryllium Sheet Rolled Flat to Gauge," Final Report, Contract AF 33(600)-35829, March 1960.
5. Yans, F. M., "Third Dimensional Ductility and Crack Propagation in Beryllium Sheet," Final Report, Contract AF(30-1)-1565.
6. Yans, F. M., Wolff, A. K., and Kaufman, A. R., "Development of Randomly Oriented Wrought Beryllium Sheet," WADD Technical Report 60-403, October 17, 1960.
7. Aeronca Manufacturing Corporation, "Development of Beryllium Composite Structures," Contract AF 33(616)-7050.
8. Giemza, C. J., "Relation of Mechanical Behavior of Beryllium Sheet to Fabrication Variables," Final Report, Contract AF 33(600)-40648, March 1961.

TABLE 1
MECHANICAL PROPERTIES OF ZONE REFINED
SINGLE CRYSTALS PRODUCED BY THE FRANKLIN INSTITUTE

NO. OF PASSES	ORIENTATION	REDUCTION IN AREA	GLIDE STRAIN	ELONGATION IN 3/8"	CRITICAL RESOLVED SHEAR STRESS
5	Basal Plane 20° to Tension Axis	20%	60%	25%	1100 psi
8	Basal Plane 45° to Tensile Axis	45%	156%	56%	520 psi

TABLE 2
CHEMICAL ANALYSIS OF BERYLLIUM

	ELEMENT, ppm				
	Fe	Ni	Cr	Mn	C
PECHINEY FLAKE	140	45	6	15	
VACUUM MELTED FLAKE	275	100	10	20	20
SUPER PURE PECHINEY FLAKE	45	8	35	5	
<u>DISTILLATION NO. 5</u>					
BOTTOM	<5	<2	<2	<5	30
MIDDLE	<5	<2	<2	<5	
<u>DISTILLATION NO. 6</u>					
BOTTOM	4.0	1	3	<5	35
MIDDLE	2.5	2	2	<5	<10
TOP	3.5	5	<1	10	
<u>DISTILLATION NO. 7</u>					
BOTTOM	1.5	1	<1	5	
MIDDLE	3.0	1	1	5	
TOP	3.0	4		15	

TABLE 3
MECHANICAL PROPERTIES OF UNALLOYED BERYLLIUM SHEET
UNDER VARIOUS CONDITIONS OF FABRICATION

ROLLING TEMP (°F)	ROLLING REDUCTION	FINISH PASSES	0.2% OFFSET YIELD STRENGTH (psi)	ULTIMATE TENSILE STRENGTH (psi)	PERCENT ELONGATION
1800	1.5 : 1	NONE	30,200	49,100	3.6
1800	3 : 1	NONE	35,100	61,600	10.9
1800	6 : 1	NONE	42,000	67,300	8.0
1600	1.5 : 1	NONE	38,600	59,800	5.8
1600	3 : 1	NONE	41,000	71,600	16.1
1600	6 : 1	NONE	37,700	65,300	16.6
1400	1.5 : 1	NONE	42,800	63,600	6.3
1950	3 : 1	NONE	32,300	61,800	11.3
1950	3 : 1	5% at 1400°F	30,400	55,300	6.9

TABLE 4
MECHANICAL PROPERTIES OF Be-1w/o Cu ALLOY SHEET
UNDER VARIOUS CONDITIONS OF FABRICATION

ROLLING TEMP (°F)	ROLLING REDUCTION	FINISH PASSES	0.2% OFFSET YIELD STRENGTH (psi)	ULTIMATE TENSILE STRENGTH (psi)	PERCENT ELONGATION
1800	1.5 : 1	NONE	44,000*	59,000*	4.6*
1800	3 : 1	NONE	42,300	66,400	8.2*
1800	6 : 1	NONE	51,300	72,200	10.2
1600	1.5 : 1	NONE	54,500	63,000	2.5
1600	3 : 1	NONE	52,500	76,600	10.1
1600	6 : 1	NONE	57,000*	81,300*	17.2*
1400	1.5 : 1	NONE	59,800	69,700	2.9
1950	3 : 1	NONE	41,900*	70,900*	11.2*
1950	3 : 1	5% at 1400°F	43,600	70,600*	10.2*

* AVERAGE OF TWO TESTS

tained through annealing vary between 1.0 and 1.77 percent with the optimum annealing cycle indication of 1050°C for 0.1 hour.

From this discussion it immediately becomes apparent that although both hot-upsetting and high temperature annealing seem to alleviate the preferred orientation problem, the latter is more conventional and appealing. We can foresee the difficulty which arises with respect to sheet size limitations in the hot-upsetting technique. However, the information obtained through this investigation is extremely valuable. Investigation in a new AMC sheet rolling program will utilize the above information, and provisions are being made for the adaptation of the annealing technique developed. A thorough and comprehensive evaluation of this added feature is programmed.

Evaluation of Structural Integrity

To determine the structural integrity of the bidirectionally rolled sheet produced, many programs have been designed to fabricate and test structural components. These programs have been initiated on theoretical formability, mechanical and physical property evaluation, crack propagation studies, design criteria, coatings, high energy forming processes, etc. Bidirectionally rolled sheet has been supplied to many aircraft companies and research organizations for evaluation under these programs. An example (7) of some of the aforementioned forming and testing that is being accomplished is shown in figure 4.

Results reported from these investigations are as yet very limited and conclusions cannot be drawn. One of the most comprehensive investigations on structural evaluation is in process at the Martin Company (8). The objectives are: to establish a standard measure of merit for characterizing so-called structural beryllium and to determine experimentally the relative superiority of beryllium, in the structural sense. An evaluation is being conducted utilizing hot-upset, hot-pressed, and hot-pressed bidirectionally rolled sheet. Mechanical property evaluation will involve bend tests, notched and smooth tensile tests, bulge tests, compression, and box beam structure testing. Specimens of varying widths and gauge thickness will be used in the bend ductility testing.

Although the evaluation is not complete, considerable progress has been made. Box beams have been fabricated from all three sheet materials and tested by constant moment bending until fracture. The beam and fracture data are shown in figure 5. The designations are: bidirectionally rolled, hot-pressed and hot-upset. Until all the evaluations are complete and the data compiled and correlated with tests and materials, we cannot draw any concrete conclusions concerning the structural merit of beryllium sheet.

Future Recommendations in Beryllium Research and Development

Even with the brief review presented herein, we can readily see that many areas of beryllium research and development necessitate further investigative effort. In addition to problems discussed, attention must also be given to the compilation of design data and, ultimately, testing of structural components for actual use in specified systems. Although, the most promising developments concerned with ductility are centered around purification, further evaluation for conclusive proof that this is the answer and that reproducibility is assured must be accomplished. Results on the single crystal work must be confirmed and the feasibility of zone refining must be substantiated by similar results on polycrystalline material. Once these are resolved and the cause of impurities is isolated, concentrated effort may be expended on developing techniques for producing the degree of purity needed on a commercial scale.

Proven success in the above programs would precipitate further efforts such as study of deformation modes and characteristics, recrystallization and grain growth behavior, alloying characteristics, further development of joining methods, and evaluation of physical and mechanical properties of the high purity material.

If the above course is pursued, another aspect for consideration is the possibility of limited improvement or negative results through purification of beryllium. This would, in effect, dictate the need for a critical review of the basic research effort, and the initiation of new programs designed to answer questions of a more developmental nature. These programs would include studies on the effect of BeO content and distribution on the mechanical properties, aging studies to determine the cause of certain phenomena under certain conditions of time, temperature, and work, and dislocation studies because of the very nature of the data they produce. Results from all these investigations will have to be evaluated and correlated with the specific properties each imparts on the material.

The future of beryllium research and development hinges on a relatively few highly oriented studies currently under way. Yet, great strides have been made, and even more encouraging is the fact that each day more and more people connected with the research and development effort in beryllium are becoming more consistent in their reasoning and in their approaches to the existing problems.

REFERENCES

1. Herman, M., Spangler, G. E., and Hein, E., "The Preparation of High Purity Beryllium and the Study of Its Flow and Fracture Properties," Final Report on Contract NOas 59, 6242-c, June 30, 1959 to June 30, 1960.
2. "Beryllium Research and Development Program," Nuclear Metals, Inc., Contract AF 33(616)-7065.
3. Gelles, S. H., Pickett, J. J., and Wolff, A., "Some Recent Advances in Beryllium Metallurgy," Nuclear Metals, Inc., TJ-31, August 31, 1960.
4. Wickle, K.G., Armstrong, J. W., and Perrin, H. N., "Development of Beryllium Sheet Rolled Flat to Gauge," Final Report, Contract AF 33(600)-35829, March 1960.
5. Yans, F. M., "Third Dimensional Ductility and Crack Propagation in Beryllium Sheet," Final Report, Contract AF(30-1)-1565.
6. Yans, F. M., Wolff, A. K., and Kaufman, A. R., "Development of Randomly Oriented Wrought Beryllium Sheet," WADD Technical Report 60-403, October 17, 1960.
7. Aeronca Manufacturing Corporation, "Development of Beryllium Composite Structures," Contract AF 33(616)-7050.
8. Gienza, C. J., "Relation of Mechanical Behavior of Beryllium Sheet to Fabrication Variables," Final Report, Contract AF 33(600)-40648, March 1961.

TABLE 1
MECHANICAL PROPERTIES OF ZONE REFINED
SINGLE CRYSTALS PRODUCED BY THE FRANKLIN INSTITUTE

NO. OF PASSES	ORIENTATION	REDUCTION IN AREA	GLIDE STRAIN	ELONGATION IN 3/8 "	CRITICAL RESOLVED SHEAR STRESS
5	Basal Plane 20° to Tension Axis	20%	60%	25%	1100 psi
8	Basal Plane 45° to Tensile Axis	45%	156%	56%	520 psi

TABLE 2
CHEMICAL ANALYSIS OF BERYLLIUM

	ELEMENT, ppm				
	Fe	Ni	Cr	Mn	C
PECHINEY FLAKE	140	45	6	15	
VACUUM MELTED FLAKE	275	100	10	20	20
SUPER PURE PECHINEY FLAKE	45	8	35	5	
<u>DISTILLATION NO. 5</u>					
BOTTOM	<5	<2	<2	<5	30
MIDDLE	<5	<2	<2	<5	
<u>DISTILLATION NO. 6</u>					
BOTTOM	4.0	1	3	<5	35
MIDDLE	2.5	2	2	<5	<10
TOP	3.5	5	<1	10	
<u>DISTILLATION NO. 7</u>					
BOTTOM	1.5	1	<1	5	
MIDDLE	3.0	1	1	5	
TOP	3.0	4		15	

TABLE 3
MECHANICAL PROPERTIES OF UNALLOYED BERYLLIUM SHEET
UNDER VARIOUS CONDITIONS OF FABRICATION

ROLLING TEMP (°F)	ROLLING REDUCTION	FINISH PASSES	0.2% OFFSET YIELD STRENGTH (psi)	ULTIMATE TENSILE STRENGTH (psi)	PERCENT ELONGATION
1800	1.5 : 1	NONE	30,200	49,100	3.6
1800	3 : 1	NONE	35,100	61,600	10.9
1800	6 : 1	NONE	42,000	67,300	8.0
1600	1.5 : 1	NONE	38,600	59,800	5.8
1600	3 : 1	NONE	41,000	71,600	16.1
1600	6 : 1	NONE	37,700	65,300	16.6
1400	1.5 : 1	NONE	42,800	63,600	6.3
1950	3 : 1	NONE	32,300	61,800	11.3
1950	3 : 1	5% at 1400°F	30,400	55,300	6.9

TABLE 4
MECHANICAL PROPERTIES OF Be-1w/o Cu ALLOY SHEET
UNDER VARIOUS CONDITIONS OF FABRICATION

ROLLING TEMP (°F)	ROLLING REDUCTION	FINISH PASSES	0.2% OFFSET YIELD STRENGTH (psi)	ULTIMATE TENSILE STRENGTH (psi)	PERCENT ELONGATION
1800	1.5 : 1	NONE	44,000*	59,000*	4.6*
1800	3 : 1	NONE	42,300	66,400	8.2*
1800	6 : 1	NONE	51,300	72,200	10.2
1600	1.5 : 1	NONE	54,500	63,000	2.5
1600	3 : 1	NONE	52,500	76,600	10.1
1600	6 : 1	NONE	57,000*	81,300*	17.2*
1400	1.5 : 1	NONE	59,800	69,700	2.9
1950	3 : 1	NONE	41,900*	70,900*	11.2*
1950	3 : 1	5% at 1400°F	43,600	70,600*	10.2*

* AVERAGE OF TWO TESTS

TABLE 5
SYNOPSIS OF STATISTICAL ANALYSES OF YIELD STRENGTH AND ELONGATION

MATERIAL	TESTING DIRECTION	YIELD STRENGTH				STANDARD DEVIATION
		HIGH	LOW	AVERAGE	LOWEST * PROBABLE	
PHASE II						
LYB - 1081 - 86 SINGLE SHEET	LONG.	70,300	58,400	64,900	55,900	3,000
	TRANS.	74,700	58,400	64,200	54,600	3,200
PHASE III						
LYS - 1112 46 SHEETS	LONG.	77,000	50,900	64,500	47,700	5,600
	TRANS.	80,700	52,500	65,300	48,200	5,700
PHASE IV						
BLEND MATERIAL 68 SHEETS	LONG.	58,800	37,400	48,300	34,800	4,500
	TRANS.	58,300	37,800	46,000	33,100	4,300
ELONGATION IN PERCENT						
PHASE II						
LYB - 1081 - 86 SINGLE SHEET	LONG.	19.0	5.0	11.7	4.4	
	TRANS.	27.3	5.5	15.4	5.9	
PHASE III						
LYS - 1112 46 SHEETS	LONG.	44.0	4.0	17.2	8.1	
	TRANS.	34.	2.0	16.0	6.3	
PHASE IV						
BLEND MATERIAL 68 SHEETS	LONG.	19.5	3.5	8.8	3.5	
	TRANS.	22.0	2.5	8.8	4.5	

* BASED ON THREE (3) STANDARD DEVIATIONS TO INCLUDE 99.73 PERCENT OF ALL POSSIBLE VALUES.

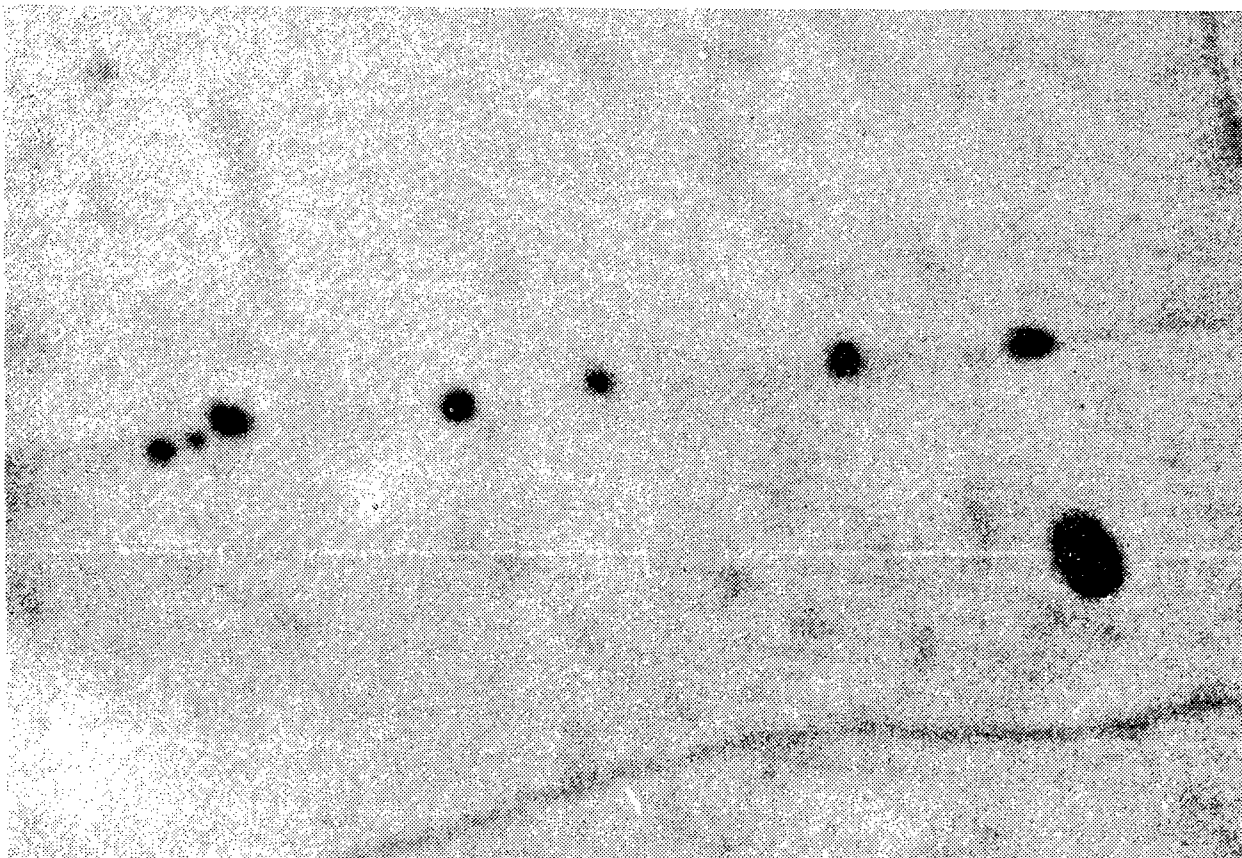


Figure 1.

ULTRASONIC WELD

Between Two Sheets Of 0.012-In. Polarized Light-100X

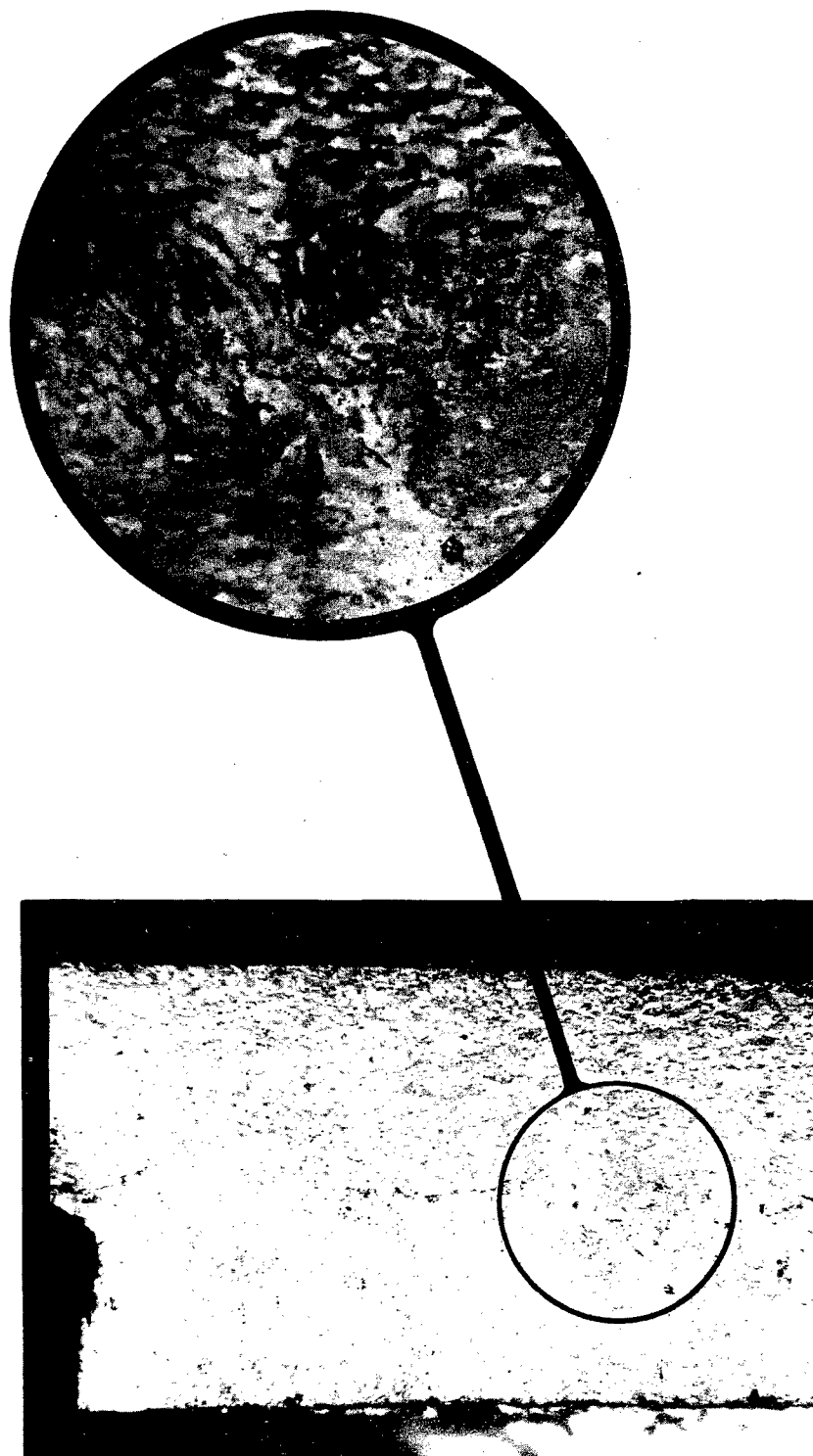
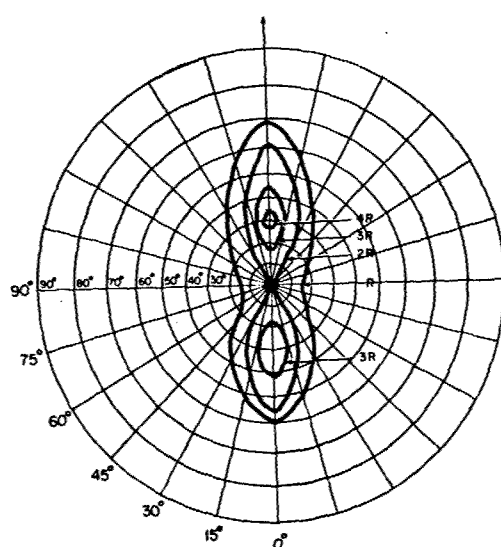
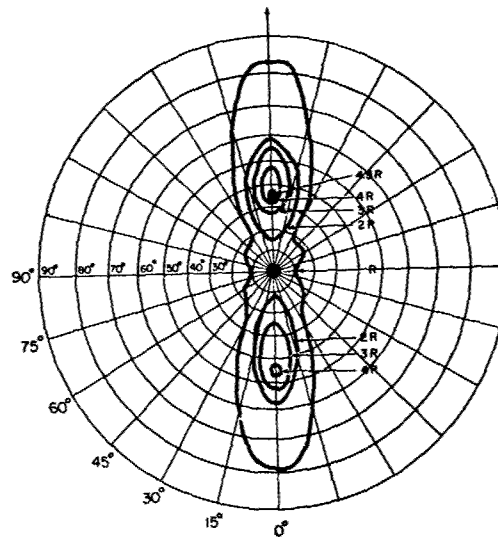


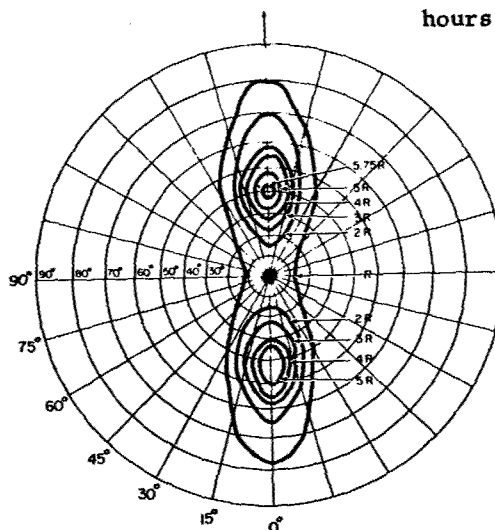
Figure 2.



(a) (0001) texture of as-rolled sheet



(b) (0001) texture for sheet annealed at 1050°C for 10 hours



(c) (0001) texture for sheet annealed at 1100°C for 22 hours

Figure 3.

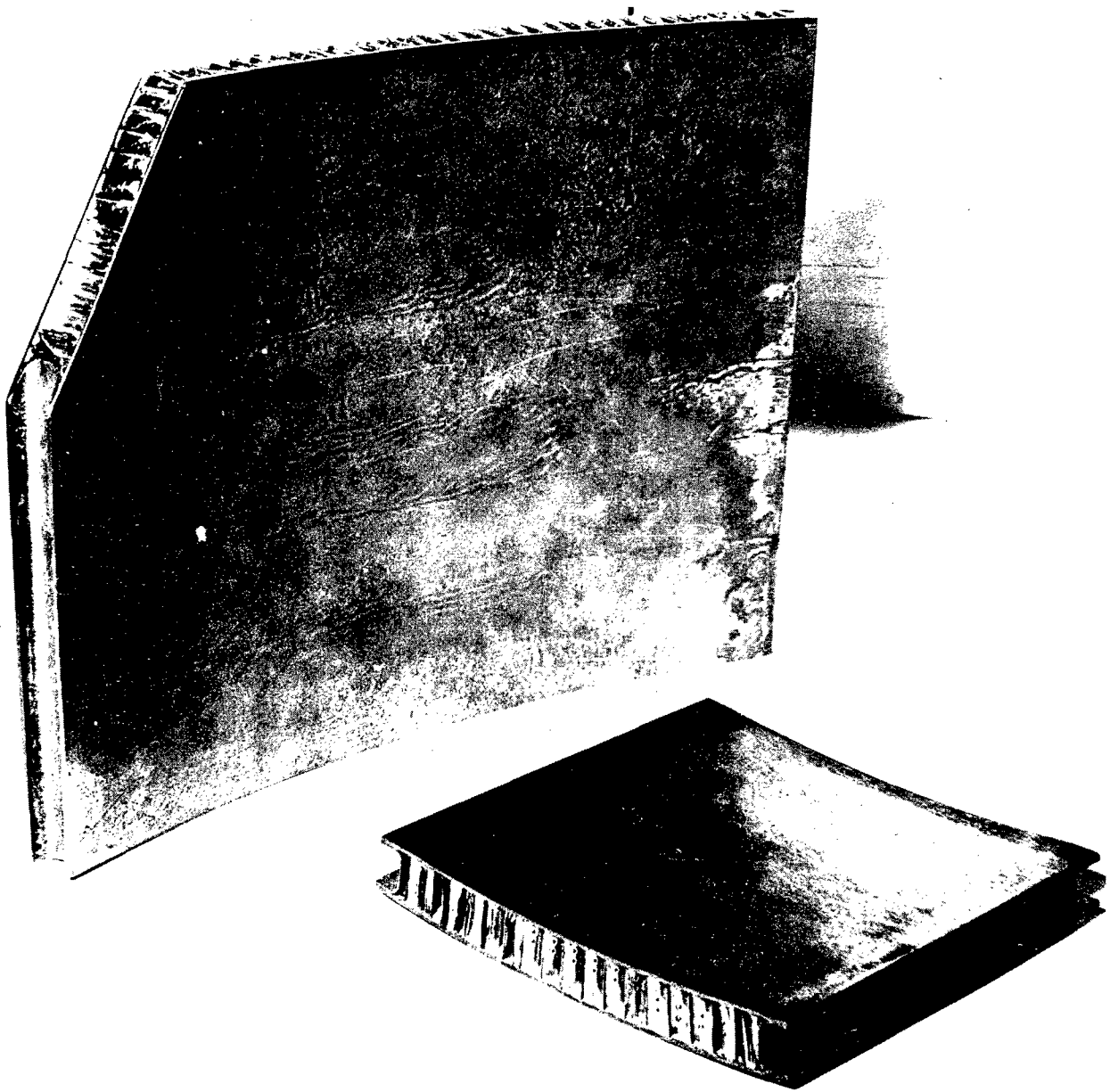


Figure 4.

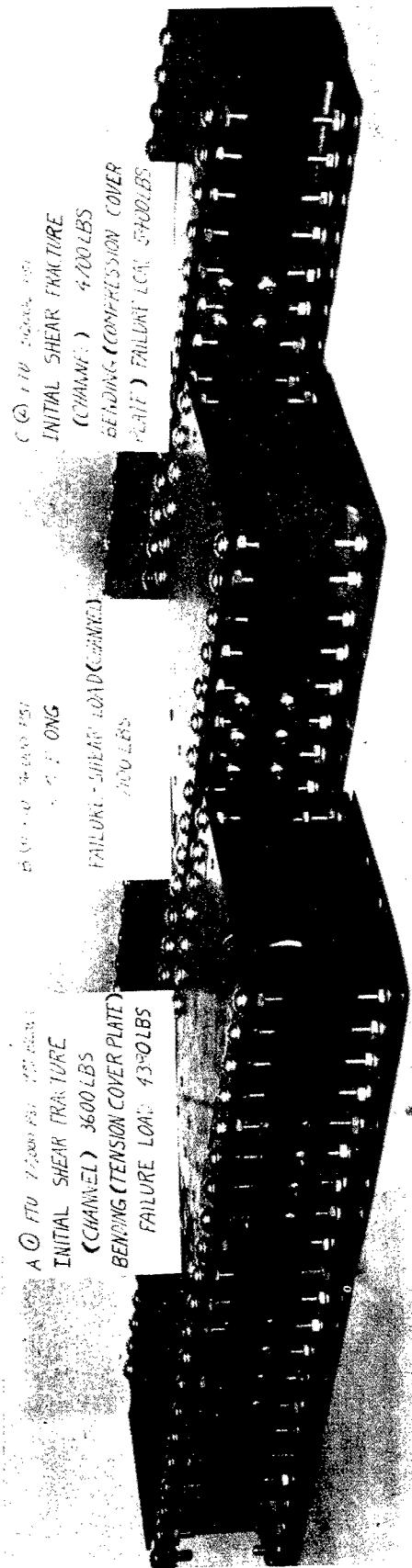


Figure 5.

SEMICONDUCTOR AND SUPERCONDUCTOR MATERIALS

Chairman

Mr. H. V. Noble

Speaker

Mrs. E. Tarrents

Panel Members

Mr. C. E. Ryan (AFCRL)

Mr. W. G. Field (AFCRL)

Lt. F. Shepherd (AFCRL)

MATERIALS FOR MOLECULAR ELECTRONICS

Elizabeth H. Tarrants

Electronics Technology Laboratory, ASD

The words "molecular electronics" have become household words in recent years, but the definition of these words can become extremely tricky. The definition that strikes at the basis of the matter says molecular electronics is "the synthesis of matter with pre-determined electronic properties so that under particular stimuli the matter exhibits complex and complete electronic functions previously performed by distinctive combinations of active and passive components." (1)

To realize the full potential of the concept of molecular electronics, three areas of endeavor must be mentioned. These areas are materials, the discovery and use of physical and electrical phenomena to perform electronic functions, and the techniques for fabrication of reliable, complex functional blocks.

It is not the intention of this paper to enumerate or debate the potential advantages of the molecular electronics concept. Nor is it intended to discuss the more familiar aspects of solid state materials and phenomena, but rather to review some of the newer approaches to solving the problems encountered in solid state electronics.

The material of interest in molecular electronics is a single crystal. For airborne applications, the greatest efforts have been in silicon, with some in germanium, followed by gallium arsenide and others of the III-V compounds.

It was only natural and most expedient that the beginnings of molecular electronics should be based on the well-known semiconductors and their technologies. However, the concept of molecular electronics must necessarily embrace all materials that have even a remote chance of being useful for performing electronic functions. The expansion into the areas of light utilization and thermoelectricity as well as other fields of application has led to new interest in expanding the list of useful electronic materials. Obviously many arrays of inorganic compounds with predictable properties can be drawn from the elements and the large number of common stoichiometric ratios.

Such an array of compounds, related to the periodic chart, serves a very useful purpose in the selection, preparation and estimation of properties of semiconducting compounds. Many compounds included in the arrays may not exist. If the compound does exist, the value of its melting point, energy gap and electron mobility, generally fits into a uniform pattern related to adjacent compounds. The crystal structure of semiconducting compounds has been shown to be of second order importance in preparing arrays. Grouping semiconductors by crystal types loses overall relationships that exist between many compounds. The reasons for the lack of data on these compounds is not that workers in the field are unaware of the large number that exist, but rather the lack of experimental work confirming the existence of a large number of suspected semiconducting compounds. (2)

For the tailoring of materials, the arrays of compounds offer an excellent starting point. The energy gap, physical, and electrical properties can be changed in a controlled manner by the addition or subtraction of one or more atoms. In the ideal situation, the device engineer would list the desired properties for a material for a particular application, then the chemist and physicist would prepare and optimize such a material.

In recent years interest has been building in the electronic behavior of organic materials. This is a logical extension of scientific endeavor, since the number of possible atomic combinations, molecular structures and physical properties attainable in organic chemistry is very large. A great amount of experimental work has been carried out on organic materials of dubious purity from a semiconductor viewpoint. As a result much data of questionable value has been accumulated on the electrical properties of organic materials.

It is not expected that any exotic devices fabricated from organic semiconductors will be available for some time. However, some of the pyropolymers appear to be medium quality semiconductors, that is, by one researcher's definition (3), material having an electron mobility in the range of 5 to 500 cm/volt-sec, which places them in the same class with tellurium, selenium, diamond and silver chloride. There are a number of unsolved puzzles in trying to reconcile theory and experimental data in the organics. For example, the calculated activation energies for some of the compounds are an order of magnitude higher than any observed values. The usual band theory predicts that the conductance of the liquid compared to the conductance of the solid should be less than one. However, the organics differ by 1000, 10,000, or 15,000 times with the liquids conducting better than the solids.

The ultimate relevance in this field comes in the understanding of the function of structure in determining the particular chain of reactions that take place. It is hoped that an understanding of electron transfer processes in the simplest of organic single crystals cannot fail to reveal the basic mechanisms of electron transfer through an ordered array. This information will be invaluable to the field of bionics and can contribute significantly to the uncovering of additional electronic phenomena. There is a crying need for the correlation of the data of the chemists, the biochemists and the measurements of the physicists in the organic semiconductor fields.

The paramagnetic, ferroelectric and ferromagnetic materials can all make significant contributions to the total concept of molecular electronics. Devices fabricated of paramagnetic materials are being used as amplifiers and oscillators, in addition, to the use of the materials in LASER and MASER applications. The most advanced use of ferroelectric devices are as active elements in parametric and harmonic generators. The thin film form of the ferroelectrics used as an active element is arousing great interest. Devices of ferromagnetic materials are used actively as frequency multipliers and as Suhl amplifiers. In addition, both the ferroelectrics and ferromagnetics are used passively as phase shifters and crystal protectors.

These materials are all useful to molecular electronics only when the physical and electrical phenomena of the materials are used to perform electronic functions. This is the key on which significant advances in the state of the art must depend.

There are approximately one hundred fifty known solid state phenomena (4). Of this number about 80 percent are unique phenomena and about 80-90 percent of the unique phenomena are useful. This means there are approximately one hundred phenomena which can be used to perform electronic functions.

The first step in the phenomena phase is to learn the types of functions which are needed. This can be determined by a study of circuits, subsystems and systems aimed at delineating possible functional blocks. Then the processes of creative thought based on the knowledge of the materials and phenomena are applied to develop a functional block which will do the job.

Some devices operating on unusual phenomena of solid state materials have been described. Experimental work is under way on a tunnel emission amplifier; a magnetic domain interaction amplifier; and a device called a neuristor. The tunnel emission amplifier utilizes conduction by majority carriers and theoretically should have extremely high frequency capabilities. The magnetic domain interaction amplifier has the potential for handling low level input signals; the ability to function at elevated temperatures and at a low noise level. The neuristor is a proposed device which propagates a discharge wave of constant amplitude, at a constant velocity and with a finite refractory period during which it is incapable of being triggered. The discovery and exploitation of these phenomena leading to the feasibility of solid state detection, amplification and generating devices operating in the microwave frequency spectrum will provide a unique capability in the fields of communications, navigation, guidance and fire control.

In the past much emphasis has been placed on the high temperature properties of solid state materials. Recently, investigations of physical and electrical phenomena at cryogenic temperatures have been started, and attempts made to establish techniques for applying cryogenic principles for device and circuit improvement. Phenomena exhibited only at very low temperatures may be useful in the design of low noise detectors, for harmonic generation, frequency mixing, low noise amplifiers, or computer elements. The cryogenic property of superconductivity has been used to demonstrate a tunneling type device which is potentially capable of operating as a very high frequency low power oscillator, a computer element or as a high frequency low noise amplifier.

Some of the more familiar phenomena such as piezoelectricity are forming the basis for new and useful devices. At the New York meeting of the IRE in March, Dr. D. L. White of the Bell Telephone Laboratories described a new ultrasonic transducer for use at microwave frequencies. Its frequency range extends from near 300 mc to perhaps higher than 10,000 mc. The electromechanical coupling is due to piezoelectricity in a material which is simultaneously an extrinsic semiconductor. All the III-V compounds are piezoelectrics as is cadmium sulfide. (5)

There are the photo-phenomena, thermoelectric properties, magnetic properties as well as the more familiar phenomena of rectification, and amplification that need to be exploited and used to the fullest. The combination of two or more phenomena to perform a single function or series of functions becomes a fascinating exercise. Such a complex begins to fulfill the true concept of molecular electronics.

The important point is that the uses of solid state phenomena can be and should be extended to create the functions required to construct electronic systems. The inevitable result will be new functions, which in turn will augment the repertory of the system designer.

The materials will be made available, the phenomena will be described and it now remains to develop the techniques and processes whereby the properties of the materials can be made available in the best possible form.

Control is the key word which links processing techniques with molecular electronics. In the past semiconductor device structures took form in accordance with the existing technologies. The development of each new fabrication method and combinations of methods permitted the exploration of broader device applications. As a rule, all of the useful semiconductor process tended to require large amounts of time to yield a complete structure capable of satisfactory electrical performance.

Recently attention has been focused on the field of semiconductor technology in an attempt to solve the problems of the expanding field of molecular electronics. Efforts expended on solid state circuits, functional electronic blocks, thin film circuit functions and integrated circuits have stressed the need for more sophisticated process tools.

The dendritic technique for forming single crystal ribbons has received a great deal of attention in the last few years. This technique has its greatest value in the elimination of processing steps, thereby, decreasing costs, increasing yields and giving greater uniformity of devices. There is an outgrowth of the dendrite technology that is even more exciting than the original process. It has been demonstrated that webs or sheets of material may be grown by a simple modification of the dendrites process. With very little attempt at controlling the growth parameters, sheets of silicon have been grown that are single crystal, have no twin planes, and have the good surfaces associated with dendrites. At this writing, 1 cm-wide sheets, 5- to 35-mils thick, without twin planes have been grown. Sheets up to 3 cm in width with one or more twins also have been grown. Evaluation of this material along with studies of parameter control are in progress. Semiconductor material of good quality in sheet form stirs the imagination. Immediately its application to large area devices and solar cells is apparent, and it has real possibilities when applied to integrated circuitry and functional blocks.

The use of thin metallic and dielectric films as passive devices is quite common, but a combination and refinement of these are the basic techniques for the newer tunneling functions. The thin film technique is being extended to include other solid state materials and particularly the semiconductors. Single crystal thin film junction devices will be especially valuable to integrated circuitry when combined with other active and passive elements. In addition to the small size and weight of thin films, this technique could facilitate the use of phenomena which may be unique with films or are masked by the bulk material.

The technique of epitaxial crystal growth has proved to be most useful and is being extended to the newer materials. This technique will be useful not only for fabricating new devices but for highly desirable improvements in old devices. Epitaxial growth makes possible graded energy gap devices, potentially better solar cells, and has been used successfully with mixed intermetallic compounds.

Techniques for preparing solid state materials such as vapor and vacuum deposition, vapor and solution growth, vapor phase reaction and transport, flame fusion and hydrothermal methods are being extended, modified, and improved. The areas of electrochemical and electron beam techniques promise significant improvement in the formation and control of junctions.

Many funds and great efforts have been expended on investigating and attempting to understand the surfaces of solid state materials. Many methods of protecting surfaces have been proposed but always these methods have been a passive treatment. That is, devices are given the final etch and washing and then a "gunk", inert gas or a vacuum are used along with a hermetically sealed can. These procedures have served for a while although the techniques for encapsulation left much to be desired in operating performance and reliability.

With the advent of molecular electronics and functional blocks, the problems of surfaces become even more challenging. Several approaches are being pursued but the most promising have in common an active ambient principle. That is, the protection of

the surface is achieved by deactivation or trapping, of mobile ionic species by reaction with a suitable chemical sink. These techniques offer surface stabilization, improvement of device yield, reliability, reduction of costs and size, and the thin film, hermetic sealing of large surface area devices. The protection of integrated circuits, functional blocks, electroluminescent devices and solar cells are areas of potentially useful applications.

The primary purpose of this paper has been to emphasize the interdependence of the areas of materials, phenomena and techniques in achieving the potential offered by the molecular electronics concept. The efforts to develop a new electronics materials technology based on the synthesis of materials with tailored electronic properties; to exploit and develop new or enhanced physical and electrical properties of solid state materials; and to develop the techniques to combine the materials and phenomena into functional electronic units that will amplify, detect, oscillate, or otherwise perform as an active device together with associated passive devices must all be pursued concurrently. To divorce one area of effort from the other will do real damage to the whole. With the increased dependence of weapons systems on electronics and the increased emphasis on reliability of molecular electronics promises to meet many requirements for advanced systems. However, considerable additional effort needs to be expended to obtain data on modes of failure rates, and a correlation of this data with materials, phenomena, applications, techniques and processes information.

To achieve the advantages offered by the molecular electronics concept, all the disciplines of the scientific world must be utilized to solve the difficulties and attain the necessary revolutionary breakthroughs. All aspects of the problem must be considered and particularly the relationship of each phase one to the other. The coordinated efforts and results of basic and applied research, electrical and electronic engineering, device and system design are required to provide a capability in molecular electronics.

REFERENCES

1. H. V. Noble, Trip Report, dated 11 May 1959.
2. A. J. Cornish, Scientific Paper 8-1038-P56, Westinghouse Electric Corporation.
3. H. A. Pohl, Plastics Laboratory, Princeton, New Jersey.
4. E. J. Scheibner, Georgia Tech. AF33(616)-6028.
5. D. L. White, Bell Telephone Laboratories.